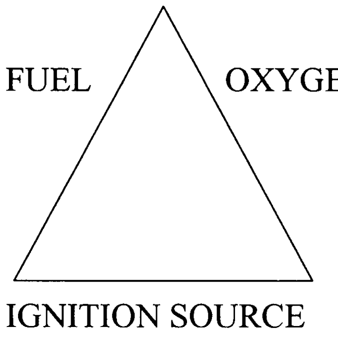
WESTERN REGION GAS CONFERENCE August 26 and 27, 2008

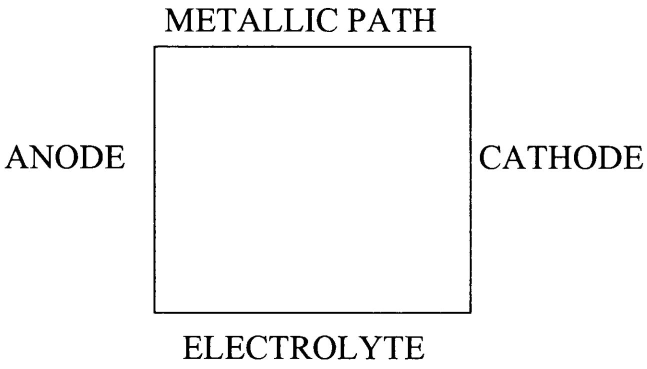
Corrosion 101 August 26

Speaker: John Brodar PE, Salt River Project

09:00 AM **Basic Corrosion Made Clear as Mud**
10:00 AM **Free Samples: Let's Make Rust**
11:00 AM **Lets Stop Rust: CP with a Dab of Coatings**



FIRE TRIANGLE



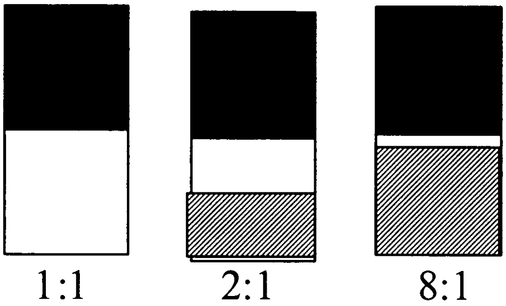
CORROSION RECTANGLE

Figure 1: Just as Fire requires all three conditions (Fuel, Oxygen and an Ignition Source) to burn, several conditions must be present for Corrosion to occur. Corrosion requires an anode, a cathode, an electrolyte and a metallic path connecting the anode and cathode. If any one of these conditions is not present or prevented corrosion will not occur. Corrosion is electrochemical in nature: the electrolyte and metallic path are necessary for current to flow. If there is no current flow there is no corrosion.

The four metals most commonly used underground and their typical potentials (relative to a Copper Copper Sulfate Reference Cell, CSE) are:

Steel or Iron	-500 to -700 mV	-.500 to -.700 Volts
Copper	-100 to -300 mV	-.100 to -.300 Volts
Zinc	-1100 mv	-1.100 Volts
Magnesium	-1550 to -1750	-1.55 to -1.75 Volts

STEEL RECEIVING CATHODIC PROTECTION IS CONSIDERED TO BE FULLY PROTECTED IF IT HAS A POTENTIAL OF -850 Mv (-.850 volts) OR MORE NEGATIVE RELATIVE TO A CSE.



AREA RATIOS

Figure 2: The 1:1 figure can represent equal areas of mild steel and stainless steel (or copper). The 2:1 figure is 1/2 shaded while the last figure is 7/8 shaded.

FIRST CASE

Assume that the black is stainless steel (or copper) and the white is mild steel. With the 1:1 area ratio an accelerated corrosive attack will occur on the white mild steel: it will have a Corrosion Unit of 1.

If we paint one half of the mild steel the area ratio changes to 2:1, there are now two time as much exposed stainless steel (or copper) as mild steel. The corrosion rate on the exposed steel will increase to approximately 2 times the Unit Corrosion Rate.

If we paint 7/8 of the exposed mild steel, almost all of the corrosion damage experienced in the 1:1 Area Ratio will now occur on the exposed 1/8 area of mild steel. The Corrosion Rate will be 8 times as great.

As we continue to coat more and more of the ANODE (the corroding structure), the intensity of the attack increases at the bare spot and pitting attack becomes more prevalent.

SECOND CASE

Paint the CATHODE instead.

Now, assume that stainless steel is white while the painted mild steel is black. The accelerated corrosion occurring at the holidays on the mild steel is due to galvanic effects. Since the mild steel is painted, this attack will have an intensity of 1P (painted or pitting).

If we paint one half of the stainless steel, we will reduce the Corrosion Rate to 0.5 x 1P = 0.5P,

If we paint 7/8 of the stainless steel the Corrosion Rate will be 0.125 x 1P = 0.125P.

If we apply a paint that is 99.99% effective we will have a corrosion rate that is only 1/10,000 P due to the galvanic effects, almost undetectable in the real world.

To achieve a successful long term soil or fresh water immersion service life the area of the exposed stainless steel (or copper) must be four or less orders of magnitude (10,000 times) less than the total surface area of the painted steel. One square cm is 1/10,000 of the area of 1 square meter.

If you compare the total surface area of this 8 1/2" by 11" paper to the area of the period at the end of this sentence the difference is five orders of magnitude.

Fundamentals of Corrosion Causes and Mitigation*

JORAM LICHTENSTEIN
Ebasco Services, Incorporated, Houston, Texas

Editor's Note: This article was volunteered following the editorial in the November, 1977 issue of MP. As a number of letters have been received from NACE members who feel that they are "being left out," it is presented here, with an invitation for other submissions.

This paper presents the fundamental causes of corrosion to underground metallic structures and control measures to combat the corrosion.

CORROSION DAMAGE in the United States costs billions of dollars each year. Research by scientists and industry has greatly expanded our knowledge of corrosion and corrosion control, and opened up a field of great opportunity for technical careers in corrosion work. Therefore, an understanding of corrosion principles and corrosion control methods should be of great interest to industry and the general public.

The purpose of this paper is to introduce the subject in general terms and provide a basic understanding of corrosion and its control.

Simple Theory of Corrosion

All metals tend to return to their natural ores as found in nature. When a steel pipeline corrodes, it is returning to the original condition of the iron ore as mined. The chemical changes occurring during this rusting process are accompanied by a transfer of electrical energy; therefore, the corrosion reaction is said to be of an electrochemical nature. This electrochemical reaction may best be explained by describing the operation of a simple flashlight battery, which is a galvanic cell.

Shown in Figure 1 are two dissimilar metals, zinc, which the battery case is made of, and a carbon rod which is the center electrode. The space between these electrodes is filled with an electrolyte which is a material that will provide the chemical reaction necessary to produce the electrical current when the two metals, carbon and zinc, are connected with a wire.

The electric current in the battery flows from the zinc into the electrolyte and then onto the carbon rod. As the current leaves the zinc, it carries small particles of metal with it, called "ions". As soon as these zinc ions are dissolved in the electrolyte, they are exchanged from ions of hydrogen which collect on the carbon rod. This film of hydrogen, if not removed, forms an insulator and tends to decrease the flow of current in the battery. Formation of this hydrogen film is called "polarization", and the removal of the film is called "depolarization".

In any galvanic cell, the electrode from which current flows into the electrolyte or solution is known as the "anode" and will be destroyed by the current flow, just as the zinc battery case is eventually destroyed by continued use of the battery. The electrode which picks up current from the electrolyte is known as the "cathode".

Several metals are shown in the following "Electrochemical" or "galvanic series" (Table 1). Each metal is anodic to the metal below it or cathodic to the metal above it. Connecting any two of the metals in an electrolyte will cause a current to flow and the anodic metal will corrode.

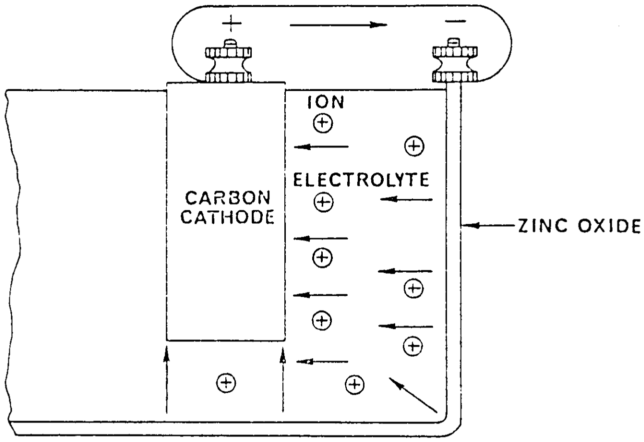


FIGURE 1 — Galvanic cell, dissimilar metal. Flashlight battery.

TABLE 1 — Galvanic Series

Metal	Volts
Magnesium	-2.34
Aluminum	-1.67
Zinc	-0.76
Iron and Steel	-0.44
Brass	-0.28
Tin	-0.14
Lead	-0.13
Hydrogen	0.00 = Reference
Copper	+0.34
Silver	+0.80
Gold	+1.36

Table 1 shows that steel will be anodic and corrode when connected to copper and placed in an electrolyte. The most rapid corrosion will occur when magnesium at the top of the series is connected to gold at the bottom of the series.

A second type of galvanic cell is when similar metal electrodes are placed in dissimilar electrolyte as shown in Figure 2. When the two electrodes are connected with a wire, electric current will flow just as was the case with dissimilar metals in the original galvanic cell.

These two cells just described, demonstrate the fundamental principle for the many known variations of the galvanic cell.

Several variations of the galvanic cell as found on pipelines will be described. Figure 3 shows an enlarged view of a galvanic cell on a pipeline. The moist earth is the electrolyte, and one area of the pipe is the anode and one or more areas the cathode. As the current leaves the anodic area of the pipe, it carries away small particles of metal called ions. These ions go into solution in the soil and are immediately exchanged for hydrogen ions, leaving the iron behind as a rusty scale or tubercle around the pit area. Sometimes the

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*Voluntary manuscript submitted for publication December, 1977.

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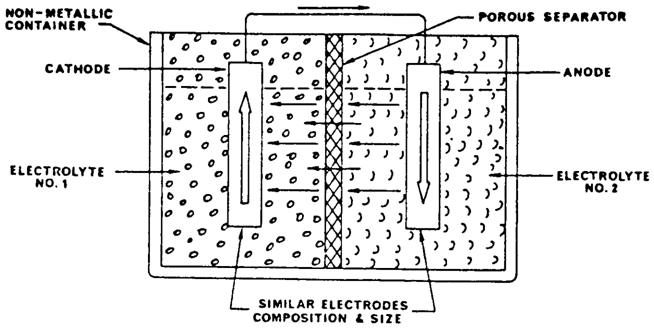

FIGURE 2 – Galvanic cell, dissimilar electrolyte.

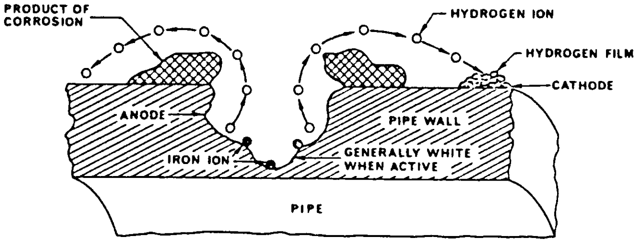

FIGURE 3 – Galvanic cell, pit action.

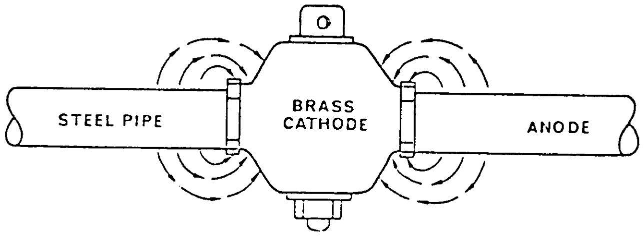

FIGURE 4 – Galvanic cell, dissimilar metals. Brass valve.

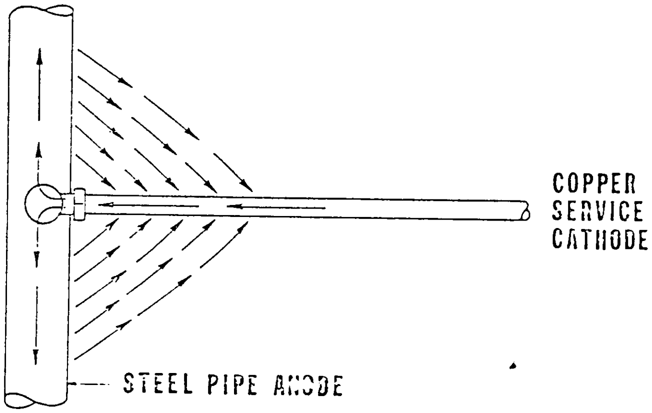

FIGURE 5 – Galvanic cell, dissimilar metals. Copper service.

barnacle-like scab will "seal off" the pit to the extent that the ions cannot get through, and the cell becomes inactive so long as the tubercle is not disturbed.

There are several common types of dissimilar metal galvanic cells. Figures 4-6 show some of the most common types.

Generally, the smaller the area of the cathode with respect to the area of the anode, the smaller the current flow and the less the anode corrodes.

Other Common Types of Corrosion

There are seven additional common types of corrosion which may be encountered in the field.

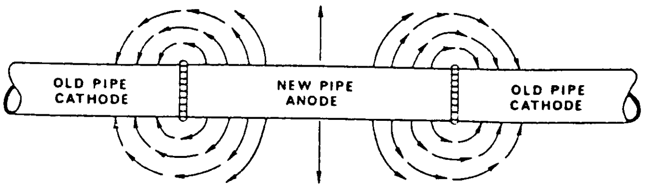

FIGURE 6 – Galvanic cell, dissimilar metals. New and old pipe.

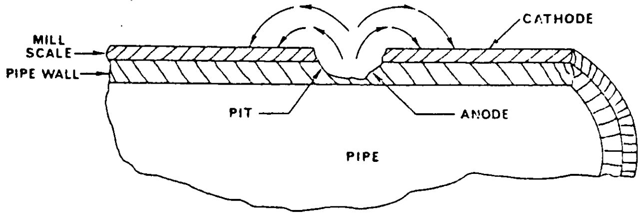

FIGURE 7 – Pitting due to mill scale.

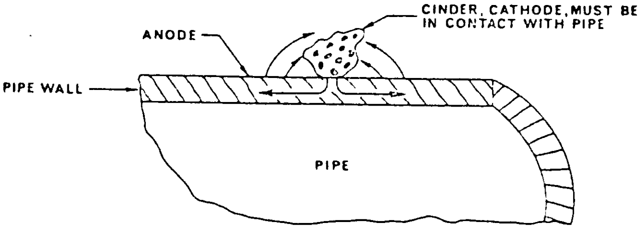

FIGURE 8 – Corrosion due to cinders.

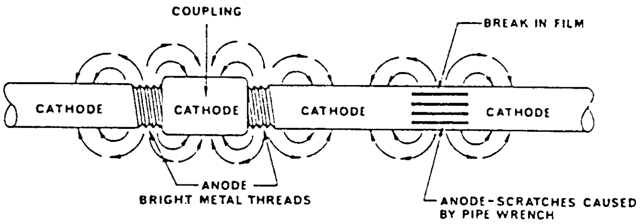

FIGURE 9 – Corrosion caused by dissimilarity of surface conditions.

Pitting Due to Mill Scale

Figure 7 illustrates this type of corrosion. During the course of manufacture, particles of mill scale may be embedded at the surface of the pipe. The mill scale acts as though it were a dissimilar metal from the pipe wall. Current in the cell will flow from the pipe, through the soil and onto the scale and return through the pipe wall.

Corrosion Due to Cinders

Figure 8 shows this type of corrosion. Cinders in contact with a pipe act as a dissimilar metal. The current flows from the pipe, through the ground and onto the cinder, and returns through the pipe wall. The acids leached out of the cinders contaminate the soil and increase its activity. No hydrogen film collects on the cinder cathode, so the cell remains active and continues its high rate of activity. This results in rapid corrosion of the pipe metal.

Corrosion Caused by Dissimilarity of Surface Conditions

Figure 9 illustrates the condition of dissimilarity of pipe surface conditions. Bright pipe metal such as scratches caused by pipe wrenches or shallow threads adjacent to couplings or fittings are anodic to the pipe surface. These cells can be very active due to the unfavorable ratio of anodic to cathodic areas.

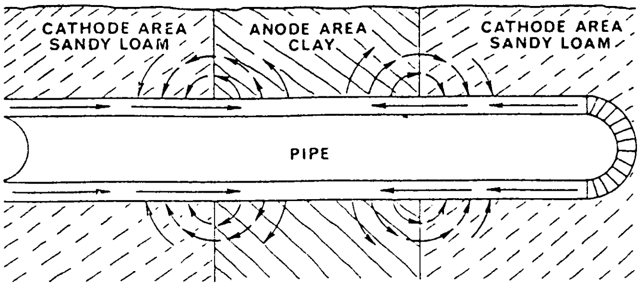

FIGURE 10 – Corrosion caused by dissimilar soils.

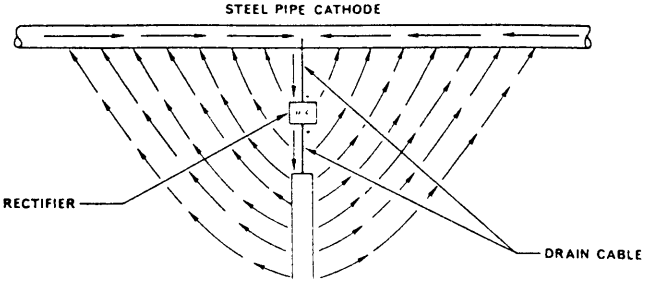

FIGURE 12 – Cathodic protection installation. Rectifier and steel anode.

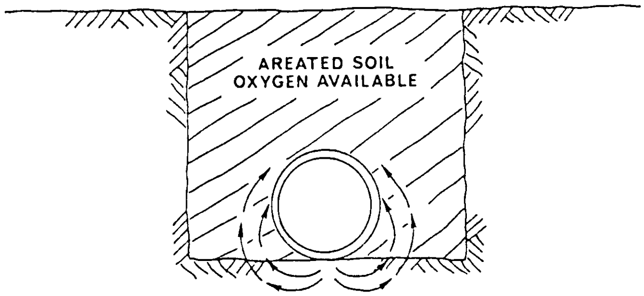

FIGURE 11 – Corrosion caused by different aeration of soil. Anodic poor or no aeration.

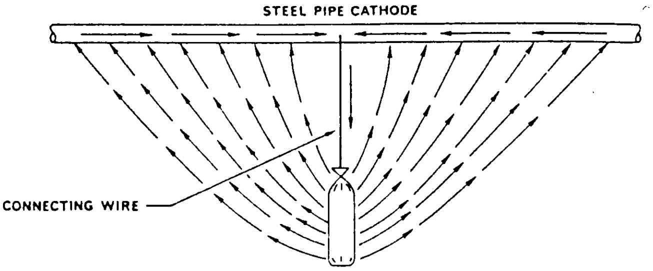

FIGURE 13 – Cathodic protection installation. Magnesium anode.

Corrosion Caused by Dissimilar Soils

Figure 10 illustrates the condition of two completely different soils or electrolytes. The rate of corrosion is determined by the resistance of the soil. If the soil resistance is low, the rate of corrosion will be rapid.

Corrosion Caused by Differential Aeration of Soil

Figure 11 illustrates the condition of a difference in aeration of soils. In this case, the soil throughout the depth of the trench is uniform, but the pipe rests on heavy moist undisturbed ground on the bottom of the ditch, while the rest of the pipe is in contact with the drier backfill. The narrow strip of pipe in contact with the bottom of the ditch is the anodic area, and the pitting can be very severe.

Corrosion Caused by Bacteria

One of the most recent discoveries in corrosion has been connected with soil bacteria. This bacteria corrosion differs from other types of corrosion in that it is caused by certain specific bacteria; that it only takes place under conditions where there is no free oxygen (anaerobic), and results in the production of sulfide as a corrosion product.

Stray Current Corrosion

In general, corrosion always takes place when a direct current (DC) leaves a pipeline and flows into the soil. Therefore, to prevent any corrosion, prevent the current from getting on the pipeline (if possible) or prevent the current from discharging from the pipe to the soil. The common methods used to prevent the corrosion are to insulate dissimilar metals from each other, apply good pipe coatings, install cables to drain the current from the pipeline back to its source when possible, apply cathodic protection, or application of a combination of these methods.

Cathodic Protection

Cathodic protection is one of the most common and effective methods of preventing corrosion. Although the principle of cathodic protection is rather simple, its application can become complicated, particularly if there are other underground structures in the area. There are two principal methods that are used to distribute the "impressed current" along the pipeline. These are the use of a rectifier and a groundbed, and the use of a metal which is anodic to the pipe such as magnesium. In both cases, the structure from which the current leaves to enter the soil and flow toward the pipeline is known as an anode.

Figure 12 illustrates a simple cathodic protection installation using a rectifier and a steel groundbed or anode. The alternating current (AC) is rectified to DC by the rectifier. The positive terminal is connected to the anode, and the negative terminal is connected to the pipeline, making it cathodic. The direction of current flow will then be from the rectifier to the anode, through the soil to the pipeline, on the pipeline to the drain cable, and back to the rectifier. The pipeline will then be cathodic and protected, and the anode will corrode. The two most common types of anodes used as groundbeds for rectifiers are steel and graphite rods.

Figure 13 illustrates a common cathodic protection installation using magnesium anodes. This method is preferred when the current requirements for protection are small, or when the installation of a rectifier station would result in a cathodic interference problem to a foreign substructure.

The combination of a magnesium anode and a steel pipe form a galvanic cell of dissimilar metals. Referring to Table 1 will show that magnesium is anodic to steel. The magnesium will corrode and the steel will be protected.

Summary

This paper and the Inco movie "Corrosion in Action" are merely an introduction to the vast field of corrosion and corrosion control. We now recognize that four basic components are required for corrosion: (1) an anode, (2) a cathode, (3) an electrolyte, and (4) a metallic return pass. Elimination or proper alteration of one or more of these components will prevent or slow down corrosion action.

For example, coatings and paints are designed to isolate the metal surface from the electrolyte; inhibitors added to the electrolyte will alter the chemical reactions in the metal surfaces; interrupting the metallic pass between dissimilar metals will eliminate the galvanic corrosion between them; and reversing the current flow direction will provide cathodic protection to the structure, etc.

This brief description of corrosion and corrosion control greatly oversimplifies both the problem and the solutions to corrosion. However, it is hoped that it will serve as a basis for understanding the process of corrosion and its control and encourage further studies of this phenomenon.

In a galvanic couple involving any two metals in this list, the normal corrosion of the metal higher in the list is likely to be accelerated while the corrosion of the metal lower in the list is likely to be reduced or completely stopped.

It will be noted that several metals are grouped in Table 2-2. The potential differences within a group are not likely to be great and the metals can be combined without substantial galvanic effects under many circumstances.

From NACE “Basic Corrosion Course”, Sixth printing 1975, Copyright 1970 National Association of Corrosion Engineers, Houston, Texas

Table 2.2 –Galvanic Series
of Various Metals Exposed to Sea Water

Active End

Magnesium
Magnesium Alloys
Zinc
Galvanized Steel

Aluminum 1100

Aluminum 6053
Alclad

Cadmium

Aluminum 2024 (4.5 Cu, 1.5 Mg. 0.6 Mn)

Mild Steel
Wrought Iron
Cast Iron

13% Chromium Stainless Steel Type 410 (Active)
18-8 Stainless Steel Type 304 (Active)
18-12-3 Stainless Steel Type 316 (Active)

Lead-Tin Solders
Lead
Tin

Muntz Metal
Manganese Bronze
Naval Brass

Nickel (Active)
76 Ni 16 Cr 7 Fe Alloy (Active)

60 Ni 30 Mo 6 Fe 1 Mn

Yellow Brass
Admiralty Brass
Aluminum Brass
Red Brass
Copper
Silicon Bronze

70 30 Cupro Nickel
G Bronze
M Bronze
Silver Solder
Nickel (Passive)
76 Ni 16 Cr 7 Fe Alloy (Passive)
67 Ni 33 Cu Alloy (Monel)

13% Chromium Stainless Steel Type 410 (Passive)
Titanium

18-8 Stainless Steel Type 304 (Passive)
18-12-3 Stainless Steel Type 316 (Passive)

Silver

Graphite
Gold
Platinum

Noble or Passive End

BASIC CATHODIC PROTECTION CONCEPTS

Explanation of Potentials

Corrosion is an electrochemical phenomenon. The corrosive behavior of steel buried in soil or immersed in water can be evaluated electrically. This is accomplished by measuring the voltage or potential of the steel compared to the potential of the surrounding earth.

This potential is frequently referred to as a "pipe to soil" potential. Any high resistance voltmeter can be used to obtain this potential. One side of the voltmeter is connected to the pipe to be measured. The other side is connected to a "reference cell". The most commonly used reference cell for field use on soil is the copper copper-sulfate half-cell or electrode ($CuSO_4$ or CSE).

The actual measurement is made on the voltage generated by two half-cells. One of these is formed by the pipe in the soil. The other half-cell is the reference cell. Together the two half-cells form one complete cell, and have a voltage that can be measured. The word "cell" is used in the same fashion as when referring to the individual cells in a car battery or flashlight battery.

Since the half-cell potential of the reference cell is constant, any variation in the measured potential must be due to the voltage of the pipe (half of the cell).

It has been determined experimentally that steel will not corrode, at ambient temperatures, regardless of pH, if it has a potential relative to a copper copper-sulfate reference cell of about -0.800 volts DC. For practical purposes, and to compensate for field conditions, this value has been raised to -0.850 volts in establishing a criteria for cathodic protection. Any steel with a potential less negative than -0.850 volts <u>may</u> be actively corroding, and requires further evaluation. See NACE document SP-01-69 "Control of External Corrosion on Underground or Submerged Metallic Piping Systems" for the complete criteria.

Common metals have different potentials. In soil these potentials have typical ranges, relative to the $CuSO_4$ reference cell:

Magnesium	-1.400 to -1.800	
Zinc	-0.900 to -1.100	
Steel	-0.550 to -0.700	(Buried in Soil or in Water)
Steel	-0.250 to -0.400	(Encased in Concrete)
Mill Scale on Steel	-0.200	
Copper	-0.100 to -0.300	
Graphite	+0.3	