CATHODIC PROTECTION OF PIPELINES

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1. History

For man, corrosion of metals has been a constant problem from the beginning of time, starting from when metals were first discovered and utilized. In fact, man learned to take the metal ore, which was in a corrosion state, and change it, converting it to the

pure metal itself. The ore being a type of corrosion of the metal was then reversed, through the use of adding energy into the ore. Therefore one could define corrosion in a general way, being the mechanism by which the metal will revert back to its original state, being the metal oxide. Thus all metals will, overtime, naturally revert back to their metal oxide. The one exception to this is gold, which is considered the noble metal.

In order to prevent or slowdown corrosion from occurring, various techniques have been developed and applied. Many of these were initially discovered on a trial and error basis. Generally coatings were the first application of corrosion prevention. The first coatings were lacquers painted on the surface of many different components as used in ancient China [1] and also the use of natural oils by many cultures throughout history [2]. The first application of cathodic protection occurred in 1825 by Sir Humphrey Davy [3]. He investigated the application of attaching various metals to copper sheets secured to the outside of British Royal Navy ships. He discovered that using iron, zinc or tin prevented the copper from corroding in seawater. This first application is currently approaching a time of 200 years prior, and formed the initial application for our current state of knowledge in cathodic protection. This was the first known record of applying galvanic cathodic protection to an engineering structure. Davy also explored the possibilities of using impressed current cathodic protection at the same time. This approach occurred after Faraday's discovery of equivalency between electrical current and corrosion [4,5], but before the equilibrium relationships as developed by Pourbaix [6]. Since corrosion is an electrochemical event it allows providing protection to a structure by electrically driving the process in reverse. Therefore by adding a second electrode and joining it to the structure to be protected, and then providing a current to the protected structure, corrosion can be prevented from occurring. These were the approaches investigated by Davy.

Buried petroleum pipelines constructed in the 1920's throughout the United States began to create serious leakage problems as a result of corrosion in the late 1920's and the early 1930's. It was a direct result of this problem of environmental contamination and product loss that in the 1930's, retrofitted cathodic protection systems on buried piping came into existence in a significant industrial way. The formation of a professional society, the National Association of Corrosion Engineers, or more commonly known as NACE, resulted in addressing the problem of corrosion prevention particularly on pipelines. In the 1940's the oil and gas industry was actively underway and cathodically protected pipelines were being installed throughout many parts of the United States. The experience and general understanding of cathodic protection was well established at this point of time and extensive use of cathodic protection was applied to new pipelines that were under construction. In addition the measurement criteria, that insured that corrosion protection was working and was effective, had previously been determined approximately 10 years earlier by Robert Kuhn [7]. In the United Kingdom cathodic protection on buried pipelines was generally not brought into play until the early 1950's. Since the initial start of cathodic protection being used in a major way, it has continued to grow for all types of applications well beyond those of pipelines. Some of the more recent applications have been in the protection of steel rebar in reinforced concrete structures and also moving towards using cathodic protection on the interior of pipelines in special circumstances. Today cathodic

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protection is a mature science and engineering application, it is well understood both in theory and operation. It is applied to nearly every critical corrosion application, ranging from pipelines to marine structures as well as chemical plant processing equipment. Although it's largest and major industrial use is in the protection of buried pipelines systems.

2. Understanding of Corrosion Protection Applications to Pipelines

The corrosion protection of a buried pipeline does not rely solely upon cathodic protection. It needs to be recognized for pipelines in particular that cathodic protection is used in conjunction with proper pipeline coatings. Thus the two methods are used in a collaborative manner whereby the joint action between the two results in good corrosion protection of the entire buried pipeline. The reasons for using both systems concurrently is primarily one of engineering economics with some degree of temporary fail safe behavior. First, if a long pipeline, many kilometers in length, were buried in an uncoated condition, a very large sized power supply would need to be installed and continually operated. This would result in very high power requirements of electricity being pumped into the ground and hence into the pipelines structure in order to provide adequate protection. Therefore the higher cost of the initial equipment and the operating cost of continually providing large amounts of current for cathodic protection would be extremely high, especially when evaluated over the long life of the pipeline. A coating system is never perfect and along the length of the pipeline there will be some pinholes or defects in the coating where cathodic protection is required. These defects or pin holes are referred to as holidays. The coating means that generally +99 % of the peripheral surface of the pipe will not require cathodic protection. This results in a much smaller sized cathodic protection system, in addition to a very low supply of current or electrical requirements. The total cost of the two systems when combined, cathodic protection and coating, results in an economical operation over the life of the pipeline. This is based upon both capital equipment costs and long term operating costs. Second, if the cathodic protection system failed or was providing insufficient protection to some locations on the pipeline, a coating system would help to maintain corrosion protection over most of the pipe. The coating thus provides the first line of defense, it allows time in which the locations where insufficient cathodic protection is occurring can be located and corrected. A major aspect of the integrity management program for a pipeline is measuring and establishing proper cathodic protection criteria along the entire length of the pipeline. Therefore areas that are found to be below acceptable protection levels can be addressed and brought up to proper levels. This is accomplished by modifications or adjustments to the cathodic protection system, thus insuring proper corrosion protection for the entire pipeline.

3. Principles of Cathodic Protection

The principle of applying cathodic protection to a corroding pipe is fairly simple. It attempts to minimize the potential or voltage difference naturally occurring between various areas on the pipe. The potential differences between these various locations are known as anodic and cathodic areas on the pipe. Cathodic protection is accomplished by providing an external anode, buried in the ground adjacent to the pipeline and inducing current flow such that the anodic and cathodic areas on the pipe are driven to

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the same common potential. At this condition individual anodic and cathodic sites on the pipe itself no longer exist. Rather now the pipe is entirely cathodic and participates in another man induced corrosion cell between the new buried anode, the soil and the pipe.

In order to understand cathodic protection, CP, and how it works one must first understand the electrochemical aspects of corrosion. These are based on two separate approaches one being founded on equilibrium conditions and the other being established upon kinetic behavior.

The equilibrium conditions are established first by, utilization of the Nernst equation [8] and second, by the use of Faraday's law [4, 5]. These two relationships when taken together result in an equilibrium corrosion diagram for metal and water. This is known as the Pourbaix diagram and has been established for most metal/water systems [9]. The Pourbaix diagram has a y-ordinate of potential or voltage and x-ordinate of pH. It is specific to one temperature and aqueous environment.

The kinetic conditions are based upon Faraday's law combined with the Arrhenius rate equation. The combination of these two relationships results in a kinetic corrosion diagram, known as the Evans diagram [10]. The Evans diagram has a y-ordinate of potential and the x-ordinate of electrical current or alternately electrical current density, the latter being more commonly used.

These two diagrams although unique in their own right are tied together with a commonality, both having the same parameter for the y-ordinate, that being potential. This general concept is shown schematically in Figure 1. This means that for various corrosion conditions the Pourbaix diagram gives the potential that occurs for a specific pH condition, while the Evans diagram provides a value for the amount of current occurring for the same corrosion potential condition. This can then be used to establish the level of potential and induced current that would be required in order to maintain a protective condition on the component in preventing corrosion from occurring.

There are two distinct methods of providing cathodic protection to a structure. The first method uses the principles of galvanic corrosion or a galvanic couple and is labeled as sacrificial cathodic protection. The second method is one referred to as impressed current cathodic protection. This method requires a DC power supply or rectifier, and an anodic bed with a connecting cable to the pipeline.

For sacrificial cathodic protection, the current necessary to prevent corrosion of the structure is supplied by the sacrificial anodes, often being a small billet of zinc or magnesium. In this case, the sacrificial anodes is buried adjacent to the pipe and a connecting wire between the anode and the pipe allows natural corrosion to occur on the anode with the resulting flow of current to the pipe giving it a protective condition in forcing it to become cathodic.

For the impressed cathodic protection approach, a direct current power supply is required in addition to an anode bed. The choice of material to be used for the anode is considerable, it is connected to the power supply and then the power supply in turn is

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connected to the pipe. In this case it is the external power supplied to the system that forces the pipe to become cathodic.

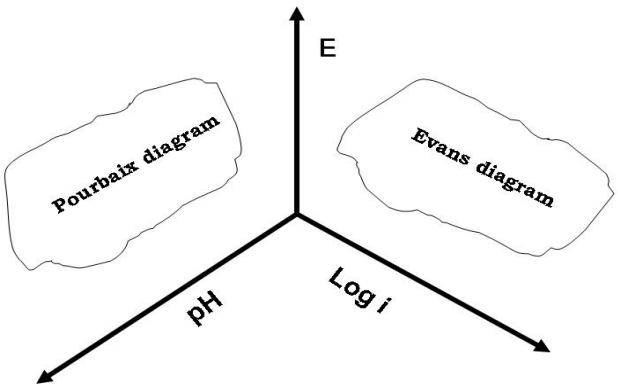

Figure 1. Relationship between Pourbaix and Evans Diagrams

The complexity in cathodic protection systems comes from the sizing of the components and placement of the anodes. These are interactively dependent upon soil conditions as well as pipeline size and coating type. The sacrificial method is used in many diverse applications including zinc and inorganic zinc coatings for atmospheric corrosion protection. However the impressed current method has one limitation, it cannot be used for atmospheric protection. The primary emphasis of this chapter is on protection of buried pipeline systems. The general concept of the two methods of providing cathodic protection is shown in Figure 2. Figure 2(a) shows the arrangement of sacrificial cathodic protection while Figure 2(b) shows the configuration for impressed current cathodic protection. As can be noted from this figure the general arrangement appears very simplistic, however the understanding of what is occurring is not.

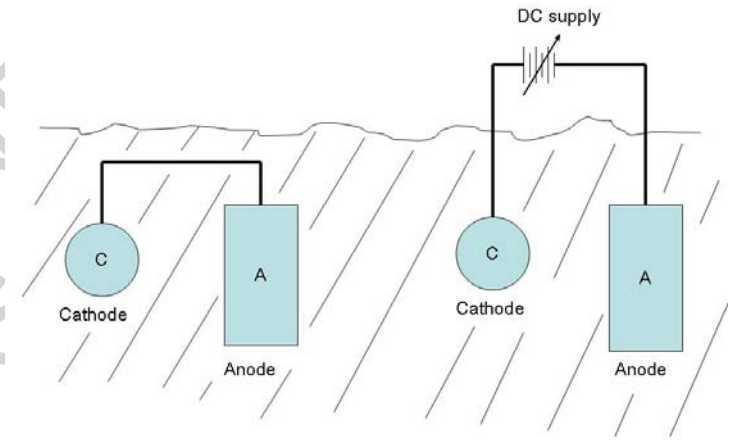

Figure 2 (a) Sacrificial CP (b) Impressed Current CP.

3.1 Corrosion Principles

For corrosion to occur on a metal surface four different elements must be present. These are, first the presence of an anode, A, second a cathode, C, third a conducting electrolyte, and fourth a conducting electrical path connecting the anode to the cathode. This is shown in Figure 3 as a laboratory identification of the four elements. These four

items when combined together constitute a corrosion cell. When these four items are present corrosion can occur, anyone of the four when missing will stop the corrosion process. The anode is where metal dissolution takes place, or where the corrosion is occurring. The dissolution reaction occurring on the metal surface is referred to as an anodic partial reaction. For steel this is described by equation 1. This specific electrochemical reaction allows the metal to dissolve and it means that current flow must occur between the anode and the cathode. Therefore the conducting electrical path between these two

$$Fe \text{ -----> } Fe^{++} + 2e \qquad (1)$$

elements allows for the flow of electrical current. The cathode is a corrosion protected element. The current flows from the anode through the electrolyte to the cathode. At the cathode another electrochemical reaction takes place. This is referred to as a cathodic partial reaction, and is where specific ions in the solution are reduced back to an element or compound. For a deaerated condition the ion that is reduced is hydrogen as described in equation 2. A balance must occur between these two reactions (anodic partial reaction and cathodic partial reaction) in terms of electrons

$$2\,H^{+} + 2e \text{ -----> } H2 \qquad (2)$$

generated and consumed. Reactions that take place specific to the anode are described as partial electrochemical reactions for the anode, or oxidation partial reactions. Similarly the description of the partial electrochemical reactions for the cathode is referred to reduction partial reactions. These two partial reactions, equations 1 and 2, show the relationship of current flow, through the presence and activity of electrons. Meaning that if two electrons are produced at the anode then two electrons must be consumed at the cathode. The flow of electrons is in fact electrical current that is flowing.

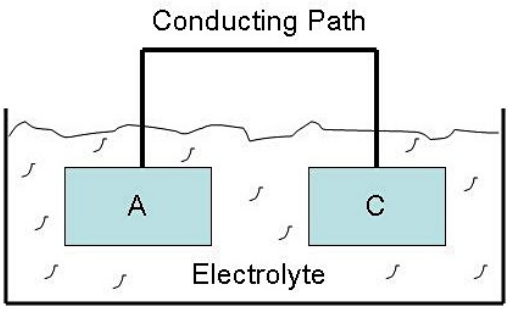

Figure 3. Laboratory Identification of the Four Corrosion Elements

Faraday established that the amount of current flowing, *I*, resulted in a directly proportional relationship to the mass, *m*, of material that was being dissolved. This is described simply as a functional relationship as given in equation 3. This means that the amount of current and the amount of corrosion are interchangeable. Therefore in any structure if one were to measure current one would get a direct measurement of corrosion. This relationship is extremely useful, as it means if we reverse the process by making the current flow in the opposite direction we can prevent corrosion from

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occurring. This is the basis behind cathodic protection.

$$m = f(I) \qquad (3)$$

Faraday's law takes into account a number of parameters in addition to the current. These include the time, *t*, atomic weight of the metal, *Ao*, the number of electrons participating in the reaction, *z*, and a constant known as Faraday's constant, *F*. Faradays constant has a numerical value equal to 96,480 coulomb/electron equivalents. The full description of these interactive parameters of Faradays law is given in equation 4.

$$m = I\,t\,Ao / z\,F \qquad (4)$$

When we measure corrosion we do so based on a rate at which the metal is dissolving. This is referred to as corrosion rate. Thus the corrosion rate is directly proportional to the current flowing. Further often it is more desirable to establish corrosion on a per unit area or on the basis of a relative thickness loss. There are many conversion factors that are applied to describing corrosion of metal systems, depending upon the specific units that one wishes to use. Normally, especially for cathodic protection systems, it is more convenient to use the current that is flowing as a parameter modified on the basis of a unit area, which is then referred to as current density, *i*. The relationship between total current and current density is given in equation 5.

$$i = I/A \qquad (5)$$

Where A is the total anodic area of the component.

3.2 Galvanic Interactions And Effects

In a buried steel structure, such as a pipeline, the soil conditions are generally close to those of being deaerated. Exceptions to this would be sandy soil or pipelines buried at a shallow depth. This means that normally little if any oxygen is present for participating in the partial reduction reaction. Therefore the dominant reduction reaction is that of hydrogen. It is important to recognize this, as later it becomes a key consideration when overcathodic protection occurs.

The conditions of the four elements as occurring on a buried pipeline are not as distinct and as easily seen as what can normally be identified in a laboratory set up. Rather the anode and the cathode both occur on the pipe and continually vary or change places, moving to different locations or positions at different moments in time. This results in general corrosion over the entire pipe surface. The arrangement of the four elements, for a buried pipeline, is shown in Figure 4. Here the soil that acts as the conducting electrolyte and the conducting path between the anode and the cathode is the pipe itself. As can be seen is not possible to remove the conducting path between the anode the cathode on the buried pipe since this path is the pipe itself.

Rather to obtain cathodic protection, a specific system is used where an additional anode is buried adjacent to the pipe, a direct current power supply is used and a metal wire is supplied as an electrical conductor between this artificially positioned anode and

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the pipe. By providing electrical power between the additional anode and the pipe, the entire pipe is now forced to become the cathode as a result of the proper direction of current flow.

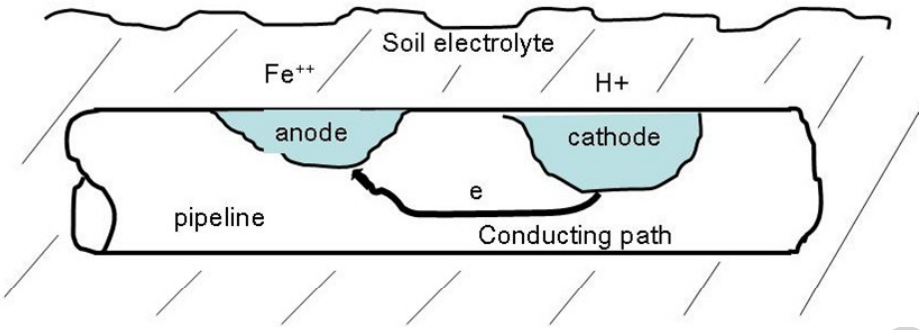

Figure 4. Corrosion Cell on a Buried Pipe

If sacrificial cathodic protection is provided then the anode material that is used must be more reactive than the material being protected. Metals are organized in a list with immune at the top and extremely active at the bottom. This list is constructed using water and is referred to as the galvanic series. The more active the metal is in terms of dissolution or corrosion, the closer it is to the bottom of the list. It also means that any metals positioned above it are less active. If two different metals are connected together then the lower metal will corrode in preference to the upper one. If the metals are close together on the galvanic scale they will both corrode, but one will corrode faster, in preference to the other. However if the metals are far removed on the scale, then the metal lower on the scale will corrode giving protection to the one above it. The scale of separation distance between the metals on the scale is one of voltage. The most negative voltage being at the bottom of the scale. The larger the difference in voltage the greater the driving force for preventing corrosion to the more positive metal. The difference between steel and zinc results in the zinc preferentially corroding over that of the steel. Thus, when the two are connected together a current flows protecting the steel. Therefore in effect, the zinc is sacrificed in preference to the steel, hence the term sacrificial cathodic protection. The two most common metals that are used as sacrificial anodes for protection of steel pipelines are zinc or magnesium.

A commonly accepted galvanic series being fairly representative of many systems in a general way is that for metals in sea water at 25°C, as shown in Figure 5. This is for a condition where a fresh metal surface is corroding. A different positioning or rearrangement occurs when an oxide forms on the surface, especially if it is naturally protective. In addition temperature and aqueous solution composition will alter the positioning of metals resulting in a nearly infinite number of galvanic series, each established according to specific conditions. Therefore the galvanic series given in Figure 5 must be used with caution.

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	Element or Material	E, mVSHE
Platinum	***Noble (cathodic)***	+ 600
	Gold	
	Graphite	
Titanium		+ 450
	Silver	
	Zirconium	
	Hastelloy C276	
	Inconel 625	
	AISI 316	
	AISI 308	
AISI 304		0.0
	AISI 410	
	Silver Solder	
	Monel 400	
	Inconel 600	
	Nickel 200	
	Mill scale on steel	
	AISI 430	
	Copper C11000	
	Red Brass	
	Bronze	
	Cartridge Brass	
	Hastelloy B	
	Tin	
	Lead	
	Cast iron	
	Wrought iron	
	Low alloy steel	
Low carbon steel		- 500
	Aluminum AA2024	
	Cadmium	
Aluminum AA 6053		- 1200
	Beryllium	
	Zinc	
Magnesium	***Active (anodic)***	- 1350

Figure 5. Galvanic Series for Metals in Sea Water Including Oxide Formation

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