Corrosion and Corrosion Control **By Jorge E. Costa and**

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ccording to a recently completed study sponsored by the Federal Highway Administration (FHWA), NACE International, and mandated by Congress in the Transportation Equity Act for the 21st Century (TEA-21), corrosion of metals costs the United States in excess of \$276 billion per year. This loss to the economy is more than the entire Gross National Product of many countries around the world. In fact, it has been estimated that 40% of U.S. steel production goes to the replacement of corroded parts and products. Our oil industries are spending more than \$2 million a day due to the corrosion of underground structures.

The study further cites that the above figure does not include indirect costs resulting from corrosion—estimated to be equal to the direct costs detailed above. Indirect costs are difficult to assess as they include the loss to parties other than owners and operators. For example, traffic delays due to bridge repairs and rehabilitation that are more difficult to turn over to the owner or operator of the structure. These become indirect costs to the user but can have a significant impact on the overall economy due to lost productivity. This is an important statistic because corrosion prevention is not only a matter of monetary savings but also has a significant impact on safety and health. Corrosion

has caused bridges to collapse, ships to sink, pipelines to explode, and has even been responsible for fatal airplane crashes. In conjunction with pollutants, corrosion has also contributed to public health hazards. Although corrosion is not a problem with a 100% effective cure, the use of current technology can diminish its damaging effects. Corrosion control measures will save our country's resources while in the process recovering billions of dollars presently being lost.

Understanding Corrosion

Corrosion is an electrochemical process whereby a material reacts to the environment in which it is placed. Generally, this process results in the loss of properties of the material, causing economic losses, affecting safety, and raising environmental concerns.

Metals corrode for a variety of reasons. Most metals are found in nature as ores and oxides, and the extraction of metals from their ores requires a considerable amount of energy. For example, iron is found in nature as ferrous oxide or iron ore. To convert the iron ore to some of the materials we know such as cast iron, stainless steel, or carbon steel, it must be alloyed with other elements. Energy is required for the alloying process and it is introduced in the form of heat. The resulting materials have a much higher energy level than when they are in their corresponding ores and will show a natural tendency to return to their natural state. The process whereby these metals return to their natural state as ores is known as corrosion.

Metals found in nature that require greater amounts of energy to convert them to useful engineering materials show a greater tendency to corrode while those that require less energy show a lower tendency to corrode. Examples of the former include magnesium, zinc, aluminum, and steel, while examples of the latter include gold, silver, and platinum.

How Metals Corrode

Being prone to corrosion is not the only condition required for the process to occur. A vehicle—known as a corrosion cell—is required to take the metal back to a lower energy state. For corrosion to occur, *Corroded reinforcing steel in concrete deck* a corrosion cell must exist. A corrosion cell consists

of an anode, a cathode, an electronic path between them, and an electrolyte.

A voltage difference between the anode and the cathode in the corrosion cell causes a current flow. This DC current flows from the anode through the surrounding environment (electrolyte) to the cathode and back to the anode through the metallic path (wire) completing the circuit. The corrosion current is carried through the metallic path by electrons and while in the electrolyte, it is carried by broken molecules known as ions. The terminal that discharges current to the electrolyte (anode) corrodes, while the metal receiving the current from the environment (cathode) remains uncorroded.

On closer inspection, it is clear that at the anode, electrons leave the surface and travel toward the cathode through the metallic path. At the cathode, the electrons reach the surface and react with various chemical species forming ions and/or molecules. The loss of electrons at the surface of the anode leaves positively charged ions. These ions react with negatively charged ions present in the electrolyte forming corrosion compounds such as ferric oxide, more commonly known as rust.

Several factors affect the strength of a corrosion cell. A greater voltage differential between the anode and the cathode, a low resistance path between them, and a high ionic concentration in the electrolyte (low resistance to ionic current flow) contribute to higher corrosion current flow, and therefore, greater corrosion rates.

While knowledge of the corrosion cell aids in the understanding of the corrosion process, recognition of corrosion cells in real world environments can be difficult. There are several types of corrosion cells, but the most common are the differential aeration cell and differential metal cell. The differential aeration cell is created when a metal is immersed in an electrolyte and is exposed to different concentrations of oxygen at its surface. The areas of the metal exposed to greater amounts of the oxygen are cathodic to areas exposed to lower concentrations. Corrosion in this type of cell occurs at the areas of low oxygen concentration. The differential metal cell is better known as the galvanic cell and it is formed when two or more different metals are placed in electronic contact with an electrolyte. Corrosion in this type of cell occurs at the metal that develops the more negative voltage in the cell (anode). Corrosion cells can also be formed on the same metal through scratches on the surface, mill scale, stresses, heat affected zones near weld areas, and even dirt or other deposits on the surface of the metal.

Corrosion Control

By analyzing the corrosion cell, it can be seen that corrosion can be controlled or eliminated

Schematic of a corrosion cell

Schematic of cathodic protection

through several methods including decreasing the voltage difference between the anode and the cathode to zero, which eliminates the current flow between the anode and the cathode; discontinuing the electric path between the anode and the cathode; and increasing the resistance to current flow in the circuit. In reality, and with few exceptions, it becomes impractical and expensive to completely eliminate corrosion; and in most instances, it suffices to reduce corrosion rates to acceptable levels. Corrosion control can be achieved with proper material selection, environmental modifications, coatings, or cathodic protection.

Materials Selection

Selecting the appropriate material for corrosion resistance is best achieved in the design stage of a project. Knowing the environmental conditions in which the material is going to be placed and its combination with dissimilar metals will help in

selecting the best-suited material for a particular application. Many times, other more important material requirements override corrosion resistance concerns and other methods must be employed to mitigate corrosion.

Environmental Modifications

An effective method for mitigating corrosion on metal structures in contained environments involves the alteration of the environment. The purpose of the modifications is to make the electrolyte less corrosive or more resistant to ionic current flow. This is normally achieved by adding certain inhibiting chemicals to the electrolyte, reducing its temperature or removing oxygen. These methods are less common and are normally confined to circumstances where there is no danger of damage to the environment by the addition of chemicals or other alterations.

Coatings

Coatings can be an effective method for combating corrosion when properly applied. Coatings are either barrier or sacrificial. Barrier coatings protect the metal by isolating it from the surrounding environment. This barrier not only physically separates the metal from the environment, but also prevents current exchange between the metal and the surrounding electrolyte. Good barrier coatings have high dielectric strength properties and withstand exposure to ultraviolet radiation, moisture, and salt. When barrier coatings are damaged, the substrate metal is free to corrode. This is why barrier coatings are generally used in conjunction with cathodic protection in submerged or buried conditions.

Sacrificial coatings also present a barrier between the metal and its surrounding environment, but in addition, they protect the metal where a damaged coating allows the metal to be exposed. This is achieved through galvanic action. Sacrificial coatings are generally metallic and are primarily produced from metals anodic to steel, such as zinc. At exposed sites, the zinc (sacrificial metal) corrodes preferentially, protecting the steel. This is also a form of cathodic protection. Examples of sacrificial coatings are galvanized and metallized coatings of zinc, aluminum, or other anodic alloys.

Cathodic Protection

In a corrosion cell, the areas of a metal discharging current to the environment corrode, whereas the areas receiving current from the environment do not corrode. Thus, if the entire exposed metal surface could be made cathodic, it would collect current and not corrode.

Cathodic protection systems operate by causing a direct current to flow from an external source to the metal structure (the anode) to surfaces of the structure (the cathode). When the current is adequate and properly distributed, corrosion is mitigated and the structure is cathodically protected.

For a cathodic protection system to work, current must be discharged to the electrolyte from an anode. In discharging current, the anode corrodes. Because the sole purpose of the anode is to discharge current, it should be made of materials that corrode slowly or do not corrode at all. Examples of the latter include dimensionally stable anodes (DSA). These anodes do not consume as typical anodes do and their dimensions remain the same as they operate during their lifetime.

Cathodic protection does not eliminate corrosion; it merely transfers it from the structure being protected to a less expensive, consumable, non-dangerous, known location—specifically, the anode. There are basically two methods of applying cathodic protection, although there are numerous variations of these methods. The basic methods are sacrificial or galvanic and impressed current.

Sacrificial Cathodic Protection

A cathodic protection system is a corrosion cell in which the structure to be protected is the cathode. Sacrificial or galvanic systems are corrosion cells of the differential metal type. Sacrificial anode systems use a material that will develop a more negative voltage when coupled with the structure of concern. Typical sacrificial anode materials include aluminum, magnesium, and zinc. When any of these anode materials is coupled to steel, they behave anodically and discharge current, which is picked up by the structure, arresting the corrosion process on the structure.

Galvanic cathodic protection systems are typically used where the total current requirement is low and the total circuit resistance allows the small voltage differential between the anode and the cathode to generate the protective current. Galvanic systems can be designed to last a long time. This is achieved by adding sufficient metal to reach the desired life. These systems also have the advantage that they require little maintenance and incur no operating costs, other than preventive monitoring and maintenance.

Impressed Current Cathodic Protection

Impressed current systems use an outside source of power to drive the current from the anodes to the cathode. This source can be solar power, batteries, DC generators or 60 Hz alternating current (AC) converted to DC via a rectifier or other device. The most common impressed current systems consist of an anode cluster (also called a ground

bed), which can be in one location or distributed around the protected structure, powered by rectified AC power.

There are many different materials to choose for impressed current anodes. Early applications used old railroad steel rails buried in the ground for the protection of buried pipelines. Anode materials include graphite rods, silicon-iron alloys and leadsilver alloys. More recent technology includes platinized titanium or niobium rods and disks, conductive graphite impregnated polymer wires, conductive paints and grouts and mixed metal oxide coatings on titanium substrates of various shapes. The latest anode technology incorporates thermal sprayed zinc and thermal sprayed titanium. These are used particularly on concrete substrates as surface conforming anodes.

Impressed current systems are commonly used where the current requirements for corrosion protection are high and where the driving voltage is greater than what can be obtained with galvanic systems. These systems are more accurate and can be controlled to deliver just enough protective current to the structure. Their disadvantage lies in that they require more maintenance and consume power.

Metallizing for Corrosion Protection

Metallizing consists of the application of a coat of metal on a properly prepared substrate. This is achieved by melting the metal and propelling it onto the surface to be coated. Metallizing, or thermal spraying as it is also known, was first developed in the 1920s, and it is a proven technology for corrosion protection, rebuilding of worn or damaged parts, dimensioning, and fabrication of metal parts and components.

When used for corrosion protection, metallizing is used to apply a protective coating to the structure surface of concern. The coatings can be sacrificial, such as zinc, aluminum and other alloys or they can be noble or cathodic. Examples of the latter are stainless steels, tin, copper and copper alloys, bronzes, and many others. When sacrificial coatings are used, in addition to providing a barrier between the structure and the corrosive environment, the coating material will protect the metal at coating deficiencies and exposed areas. Sacrificial coatings are often used in combination with sealers and barrier coatings. These overcoats are used primarily for aesthetic purposes but they also help seal the porosity that is inherent to metallized coatings and provide a degree of protection to the metallized coating from the environment. Metallized coatings provide a highly synergistic relationship with sealers and paints, because the paints are anchored on an excellent substrate and

typically last much longer than when applied directly on the steel. Cathodic coatings are chosen for their resistance to corrosion in a particular environment and they primarily act as barrier coatings. The quality of the application becomes very important when using cathodic coatings, because small defects and coating damage will cause the substrate to corrode faster since it is anodic to the coating.

The thermal spraying methods available today include flame powder, flame wire, wire arc, conventional plasma, detonation gun, high velocity oxyfuel, high-energy plasma, and vacuum plasma.

The Wire Arc Metallizing System

The process of wire arc thermal spraying consists of continually feeding two metal wires to the spray gun at a uniform rate of speed. At

Metallizing for corrosion protection of steel using wire arc system

Metallized coating formation and composition

the gun, the wires, which are electrically charged, are brought together at an intersecting point and an arc is struck between them. The heat generated melts the metal and a stream of compressed air atomizes the molten metal and propels it to the properly prepared surface. The molten metal bonds to the substrate producing a high quality, high adhesion coating. The characteristics of the resulting coating can be modified somewhat by adjusting the current output and the compressed air flow.

The wire arc system results in high adhesive and cohesive strengths, low oxide content, and low porosity. These systems demonstrate high spray rates, very low power consumption, and high-energy efficiency when compared to all other available methods, while also providing the lowest process cost. Wire arc systems are rapidly becoming the system of choice for high volume, infrastructure corrosion control applications, particularly when the project requires in-place metallization. The development of this technology, its field portability, and relative low cost make wire arc systems a viable countermeasure for the solution of corrosion problems in the field.

Compared to other techniques for corrosion control, the wire arc thermal spray coatings also show distinct advantages. Conventional paints and coatings do not provide the degree of protection that metallized coatings offer, both as barriers and sacrificially. Also, conventional coatings require frequent maintenance and repairs. Metallized coatings can substantially increase the recoat cycle, and in many instances, completely eliminate it. The initial cost of a metallized coating system may be higher than a conventional coating, but the life-cycle cost will be lower for the metallized coating. Galvanizing provides sacrificial protection to the structure but metallizing also offers several advantages over this method for corrosion control.

The nature of the galvanizing coating is such that only a thin layer at the surface is pure zinc. Closer to the steel substrate, the morphology of the galvanizing changes as it alloys with the iron. Metallized zinc coatings are pure zinc entirely, which makes the metallized zinc coating much more efficient than galvanizing because the entire coating thickness is used for corrosion protection. Further, large pieces can be difficult to galvanize in one pass, whereas they can be easily metallized after erection.

Corrosion of Reinforcing Steel in Concrete

Corrosion of the reinforcing steel in concrete is a problem that has gained much attention in recent years because of the emphasis being placed on the decaying infrastructure of our highways and bridges. In the first quarter of 2005, the American Society of Civil Engineers (ASCE) released a startling report on the status of U.S. infrastructure. Titled the "2005 Report Card for America's Infrastructure," the report detailed the results of an evaluation study by ASCE on the condition of roads, bridges, transit systems and a variety of other elements. Providing each category with a grade A through F, A being best and F being worst, ASCE gave U.S. infrastructure an overall score of D.

Concrete is a beneficial environment for steel because of its high alkalinity. This high alkalinity (high pH value), causes the steel to react and form a passive oxide film on its surface protecting it against corrosion. When the passive film is removed, the steel is subject to corrosion damage. Few conditions cause the passive film to be disrupted, the most common being the contamination of the concrete by chlorides. The source for chlorides is salt (sodium chloride). Salt is used in the northern latitudes for deicing purposes during the winter months and in coastal areas it is available from salt-laden atmospheres. Chlorides penetrate the concrete through its pores and cracks and when they reach the level of the reinforcing bar in sufficient amounts, they remove the passive film from the steel. Another, albeit less common, cause for the loss of passivity of the steel in concrete is carbonation. Carbonation is caused when carbon dioxide present in the atmosphere reacts with pore moisture and forms carbonic acid. This mild acid solution reduces the alkalinity of the concrete surrounding the steel resulting in the loss of passivity.

Once the passive film on the steel surface is compromised, moisture and oxygen then fuel the corrosion. As the steel corrodes, ferric hydroxide (rust) is produced, and its volume can be six to eight times greater than the original size of the *Corroded reinforcing steel in concrete pile*

reinforcing bar. The increase in volume causes stresses within the concrete of as much as 5000 lb/in.², causing cracks and spalling the concrete.

States, federal agencies and other researchers have invested a significant effort to determine a cost-effective solution to this problem. Results from this research have indicated that a certain level of chloride contamination is required to initiate corrosion. Once the concrete is contaminated and the reinforcing bar is actively corroding, the only method with a proven and long-term track record for corrosion control is cathodic protection. Electrochemical chloride removal and restoring alkalinity (for carbonated structures) also have a record of successful applications in Europe and North America but to a much lesser degree than cathodic protection.

Cathodic protection consists of making the entire surface of the reinforcing steel the cathode in a corrosion cell. This is achieved by placing anodes in the concrete so that they can deliver protective current to the steel. At first, impressed current systems using platinized titanium wire, conductive coatings, and other anodes materials were used. However, experience with these has been poor over time. More recently, mixed metal oxide anodes in the form of mesh and ribbon have been used with better performance. The latest developments in this area are sacrificial cathodic protection systems, including embedded zinc anodes, zinc mesh anodes, sacrificial jackets and metallized sacrificial coatings.

Metallized Cathodic Protection Systems

Metallized cathodic protection systems have enjoyed increased acceptance for corrosion protection of steel reinforcing in concrete since their introduction in the early 1980s. More than 2 million ft² of metallized anodes for cathodic protection systems are in operation in North America. The bulk of these installations use zinc as the anode material. Other anode materials in a developmental stage include aluminum-zincindium, zinc-aluminum alloys of various compositions, and catalyzed titanium. Although metallized cathodic protection systems have developed a good reputation as sacrificial systems using zinc, this technology is also used to install anodes for impressed current systems.

In a sacrificial cathodic protection system, the anode (usually zinc) is thermal sprayed onto the surface of the concrete. Contact is made to the reinforcing bar with specially designed hardware attachments. These systems do not require outside sources of power and are "self-regulating." This means the current output from the anode is primarily controlled by the resistance of the

Schematic of metallized cathodic protection system

Installation of metallized cathodic protection system on underside of deck

concrete. If the resistance is low, a condition generally conducive to higher corrosivity, the anode will deliver higher current outputs. If the resistance is higher, the opposite will be true.

Sacrificial zinc cathodic protection systems have been used successfully for the protection of concrete structures in a wide variety of environments. Metallized cathodic protection systems operating in sacrificial mode are very effective in warm, humid environments, such as marine structures and along coastal areas. These systems are currently being used for bridge substructures, piles and columns, high-rise balconies, parking garages, concrete cooling towers, concrete intake and outfall structures in power plants, dock

facilities, and more. Many State Departments of Transportation (DOTs) have standardized the use of these systems for the repair and rehabilitation of bridges and other structures.

In some applications where the concrete resistivity is relatively high, yet corrosion of the reinforcement is still a possibility, the metallized zinc anode has been treated with liquid humectants. These humectants, primarily made of lithium bromide are hygroscopic and reduce the contact resistance between the anode and the concrete. Metallized zinc can also be used as an impressed current anode for concrete structures. These systems are powered externally and permit a higher degree of control in terms of current distribution. Impressed current systems also allow the anode to overcome higher contact resistance to deliver protective current to the steel. Impressed current systems using metallized zinc as the anode are in use in intake structures at power plants, bridges, commercial buildings, and other structures. Oregon's DOT possesses what is probably the largest portfolio of metallized zinc impressed current systems, having installed the system on many bridges along the coast. These bridges, designed by the late famed bridge designer Conde McCullough, are of great architectural, historical, and aesthetic value to the state. The metallized zinc cathodic protection systems where carefully researched and tested by the state engineers before they were selected in the early 1980s as the best protective system for the local conditions.

Controlling Corrosion

Corrosion most often affects metal structures such as bridges, steel reinforced concrete, storage tanks, and pipelines. Corrosion problems often are not obvious but can lead to extensive structural failure and loss of capital investment. As the average age of facilities and structures continues to rise, corrosion problems will inevitably worsen. However, related expenses can be minimized by using proven technologies in the design, construction installation, maintenance, and repair of structures. By using state-of-the-art, proven corrosion control technology, professionals have the ability to address the decay of the infrastructure facilities and to extend the lifespan of structures for the next generation and beyond.

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