



MetalSafe Corrosion Protection Technical Presentation

CORROSION PROTECTION WITH METAL SAFE

The destruction of residential and industrial items and structures as the result of environmental corrosion is a problem of immense magnitude. In fact, it is reasonable to say that the single most important reason to paint or coat metallic structures is to prevent corrosion, and by far the largest cost impact of corrosion involves iron, and its various forms of alloys known as steel.

As a consequence of the large energy input required to extract iron from the ores in which it is found in nature, the metal forged in a steel mill is in a high-energy condition which endeavors to return to its former stable, oxidized, low energy state, whenever the environmental conditions allow. It is the energy difference between the pure metal and its oxidized forms, which is the driving force for corrosion.

All corrosion involves electrolysis and in the case of rusting steel it always involves the steel object becoming an anode in an electrolytic cell. In the case of steel rusting, the mechanism involves the presence of water acting as the carrier of the electrons shown in the equations below. Some of the cells can be extremely small – a fraction of a millimeter in size, in which the cathode (which does not corrode) is a less electropositive element such as copper. Mild steel is an impure, heterogeneous material and this is a major factor contributing to its poor resistance to corrosion. The presence of anodic and cathodic sites on the steel surface and their reaction with oxygen and water results in the transformation of a metal atom to a metal ion by the loss of electrons i.e.

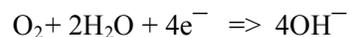
In its simplest form the anodic reaction can be written as:



Where Fe is elemental iron, e^{-} is an electron, and Fe^{++} a soluble form of iron called a cation. This indicates that at the anode neutral iron loses two electrons (i.e. becomes oxidized) and is transformed into soluble cations, which may or may not remain soluble depending on other conditions within the cell. The presence of water in the cell means however that the electrochemistry at the anode becomes quite complicated as the result of competing reactions. For example water itself can also be oxidized to give free oxygen (O_2) and acidic hydronium ions (H_3O^{+}) both of which contribute to the rapid deterioration of the iron substrate. For example:



By contrast, the electrolytic reaction at the cathode involves oxidation of water by the ‘same’ two electrons shown above, which had entered the wires of the electrical cell at the anode. But crucially, as shown in its simplest form below, the actual oxidation of water also requires access to elemental oxygen.



The overall consequence of these anodic and cathodic reactions is that the anode (iron in this case) is exposed to an acidic environment (low pH) while the cathode becomes alkaline (high pH).

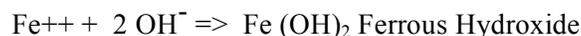
If the cell is very small, this oxygen might be supplied by the anodic reaction, but more commonly free oxygen is required to complete the electrolytic rusting of steel. The process can also be accelerated by impurities in the water. Seawater for example, not only contains dissolved atmospheric oxygen that can facilitate the reaction, but also contains almost 3% of sodium chloride that results in the formation of highly soluble iron chlorides. These chlorides are rapidly removed from the steel surface and by a competing oxidation reaction at the anode, highly destructive and poisonous elemental chlorine (Cl₂).

The most important point to be made here is that both sides of the rusting equation – anode and cathode – require access to two external fuels: water and oxygen. Even the most heavily contaminated iron will not rust unless both electrodes are exposed to sufficient quantities of water, and the cathode has access to sufficient free oxygen. If the supply of oxygen and water is denied to the surface, no corrosion can take place.

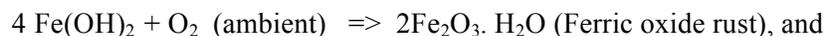
As described below, most anti-corrosive treatments involve attempts to deny these cells access to these elements. Consequently, while mild steel remains one of the most widely used industrial and residential construction material by virtue of its relatively low cost, mechanical strength and ease of fabrication. Its main drawback is that it rapidly corrodes if exposed to both water and air, particularly if the water is contaminated with reactive electrolytes such as the sodium chloride in seawater. Unless adequately protected, rapidly loses strength, which may result in structural failure.

In general terms corrosion can be defined as the spontaneous reaction between a material and its environment, which results in the degradation of that material. (The heterogeneous character of steel allows for some sites to favor the anodic reaction and for others for to favor the cathodic reaction).

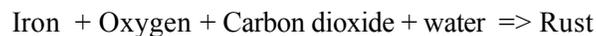
The ferrous ions and hydroxyl ions formed combine together to produce ferrous hydroxide:



The ferrous hydroxide formed reacts with more oxygen to form hydrated ferric oxide, the familiar reddish brown rust.



All of these reactions occur simultaneously and can be simply represented as:



In reality, the process is not so simple. In addition to forming the ferric hydroxide (Fe₂O₃.H₂O) shown, some ferrous hydroxide (FeO.H₂O) may also exist, in addition to various carbonates such as Fe₂O₃.(CO₂)₃ and mixed hydrates may also arise due to reaction of the oxides with carbon dioxide from the air. The rate that corrosion occurs is also highly variable and can be affected by many factors. The speed with which corrosion proceeds in proximity to seawater can be influenced by many factors including oxygen concentration in the water, pH (acidity or alkalinity), water temperature and most importantly dissolved salts such as chlorides and sulphates that can accelerate the process due to the high solubilities of the iron salts of these anions. There are also many different types of corrosion including pitting corrosion and bacterial corrosion, both of which are particularly relevant for the marine industry.

Corrosion Prevention Overview

In summary, the rate at which corrosion is able to destroy metallic iron or steel depends on a number of factors, including:

- (i) The potential difference between the iron anode and whatever cathode is completing the cell
- (ii) Temperature
- (iii) Degree of exposure to aqueous electrolytes
- (iv) The composition of soluble salts in the electrolyte
- (v) Oxygen content of the electrolyte
- (vi) pH in the immediate proximity of the anode¹

Three approaches most commonly employed to address this problem are (a) cathodic protection, (b) physical isolation, and (c) use of chemical additives.

a) Cathodic Protection

One widely used method used to retard the corrosion of ferrous materials such as steel, is to convert the entire structure being protected into a cathode. This is typically accomplished either by connecting the structure to a piece of metal such as zinc, which can be oxidized more quickly than iron. By bringing zinc in contact with iron or steel in a moist environment, the zinc becomes a 'sacrificial anode' and dissolves preferentially. The disadvantage of this approach is that the zinc must eventually be replaced. Alternately, the steel structure can be connected to an electrical power source in which certain conductive materials such as carbon or mixed metal oxides are converted into anodes using a power source. This method is widely used to protect long distance buried steel pipelines.

a) Physical isolation

By far the most common method of preventing steel corrosion of small items or structures involves isolation of the metal from contact with air and water by means of some kind of membrane or paint. Most common is the physical isolation of the vulnerable structures from a corrosive environment by means of barrier coatings. These coatings consist of various types of membranes that minimize each of these factors. Most importantly such coatings have the following properties:

- (i) Low permeability to water and air
- (ii) Low toxicity, environmental acceptability
- (iii) Non-flammable
- (iv) Ease of application
- (v) Low cost

While solvent-based products remain common, water-based membrane forming compositions are increasingly preferred for reasons of safety and cost.

In describing the chemical and physical properties essential for anti-corrosive membranes to be successful, it is also important to understand the significance of a phenomenon known as 'pitting corrosion'. It had been believed that coatings simply acted as a barrier to oxygen and water, however research has shown that oxygen and water, at a level sufficient to initiate the corrosion reaction, can indeed permeate through intact coatings. Water permeating through a coating to the steel surface can cause displacement of the coating from the steel allowing corrosion to occur. Low permeability and good 'wetting' i.e. adhesion under immersion, are the single most important aspects of corrosion control by coatings. These are two of the main characteristics of the Advanced Protective Coating MetalSafe products.

b) Anti-corrosive additives

In addition to physical isolation of the substrate, various specialty additives can be employed to enhance the performance of the membrane, or alternatively by increasing the alkalinity (pH) of the water to which the steel is exposed. Alternately, the addition of certain chemicals such as alkaline silicates that preferentially adsorb on the steel surface to restrict access to air and water are utilized as a means of enhancing the performance of the barrier coatings. Of the many such additives commercially available, the very effective sacrificial metals such as zinc and aluminum can only be employed in solvent-based anti-corrosive paints being unstable in water-based paints and coatings.

In spite of the large number of formulated products marketed to control steel corrosion, very few are capable of dealing with one of the most widespread and dangerous threats to steel structures known as pitting corrosion

Pitting Corrosion

Pitting is arguably one of the most dangerous forms of corrosion for exposed steel. It occurs as the result of widespread existence of stray electrical currents, which most commonly arise due to the induction from industrial sources such as overhead wires or stray surface currents due to charged underground structures such as pipelines or electrical cables. The problem arises because although the magnitude (amperage) of such currents are very low, the actual effective amperage on a protected steel structure can be substantially enhanced if the barrier coating is breached for some reason. Paradoxically, the vary properties required for a barrier coating to function – i.e. resistance to penetration by water or air – are largely nullified if any section of the coating suffers the smallest puncture. When a pinhole occurs, the localized current is concentrated at that spot – the smaller the pinhole, the higher the current density. This then results in rapid penetration of the structure, with potential catastrophic effects if, for example this object is a tank containing a dangerous material. As discussed more fully below, the Advanced Protective Coating MetalSafe line offers a number of advantages over other water based-corrosion inhibitors including a unique approach to the problem of Pitting Corrosion

ADVANCED PROTECTIVE COATINGS: METALSAFE PRODUCT LINE

Advantages

Extremely good water resistance

Enhancing the protective properties of a coating can also be achieved through reducing permeability and increasing its water repellent properties. Both features are achieved when MetalSafe products are applied as an ‘instant-set’ coating using the CaCl_2 solution. The Ca^{++} with the residual emulsifier creates an insoluble soap that both reduces the permeability of the membrane to water and oxygen and acts as water repellent. A common definition of waterproofing is a penetration as determined by the European test EN 1062 of $1.00 \text{ kg/m}^2/\text{hr}^{0.5}$, both MetalSafe B-300 and MetalSafe S-300 have been found to have values of $0.0002 \text{ kg/m}^2/\text{hr}^{0.5}$.

Surface does not have to be perfectly clean

A thin film of rust is actually advantageous. Emulsifiers are designed to react and neutralize small quantities of rust. Typically for maximum coatings adhesion, steel surfaces must be clean, dry and free of oil, rust, salts and other contaminants. However, increased surface roughness often associated with rust, results in a greater surface area and increased coating adhesion, particularly where the coating

has good 'wetting' properties and penetrates into all of the pores/crevices on the steel surface. The Advanced Protective Coating MetalSafe products have both very good wetting properties, and when applied as 'instant-set' using the CaCl_2 solution to break the emulsion, carry positively charged ions into the coating that contribute to improved adhesion through an ionic bonding.

The 'Self Healing' solution to Pitting Corrosion

Finally, excellent corrosion protection coatings have excellent 'undercutting' resistance, i.e.: resistance to corrosion creep under the film at areas mechanically damaged and resistance to hydroxyl ions produced during the corrosion process. The performance of MetalSafe Coatings have been demonstrated in completion of a 1200 hour ASTM B117 -97 'salt fog' test with no evidence of creep back or undercutting of the membrane/steel interface.

Two part application of B-300 using Calcium based crosslinking agents

The spray applied MetalSafe B-300 is typically applied through a two-part spray pump system in which an aqueous solution of calcium chloride (CaCl_2) curing agent combines with the product to yield a membrane that sets within seconds and is safe to be used for foot traffic within the hour. Since most of the free chloride exudes during the curing process, little remains to compromise the performance of the product. However, if the job demands a completely chloride free application, a solution of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) is readily available and is a well tested alternative.

Next Steps

For further technical and procedural information, please consult the Advanced Protective Coatings technical data sheet, application and Safety Data Sheets (SDS's) guidelines for the MetalSafe product line; July 12, 2015.

[Note 1: Which can also be affected by exposure to fresh alkaline such as fresh sea water with a natural pH of 8.2 which can retard corrosion by neutralizing the acidity in proximity to the anode.]