

CORROSION MECHANISM OF STEEL MATERIALS AND ITS PROTECTING METHODS

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- Corrosion Engineering
- Maintenance Technology
- Bridge Engineering

ABSTRACT

The main object of this paper is to clarify the corrosion mechanism of bare steel that is exposed to atmosphere. Various methods for protecting steel

materials exposed to the atmosphere against corrosion are also investigated.

1. INTRODUCTION

There is no steel found on earth in the form of a pure mineral like gold. Steel is an artificial substance made from iron ore that is stable in the form of oxide. Since steel is not stable in nature, it tends to change to a stable form of oxide whenever it is exposed to the atmosphere, water, or soil; and this is corrosion. Corrosion is the destructive attack of a metal by chemical or electrochemical reaction. Deterioration by physical causes is not called corrosion, but is described as erosion, galling, or wear. From the point of view of structural performance, corrosion is a potential cause of failure by virtue of the higher levels of stress resulting from reduced section. In order to achieve a long service life of steel structures, proper protection methods of steel against corrosion are necessary. This requires a good understanding of corrosion mechanism of steel materials.

2. CORROSION MECHANISM OF STEEL MATERIALS

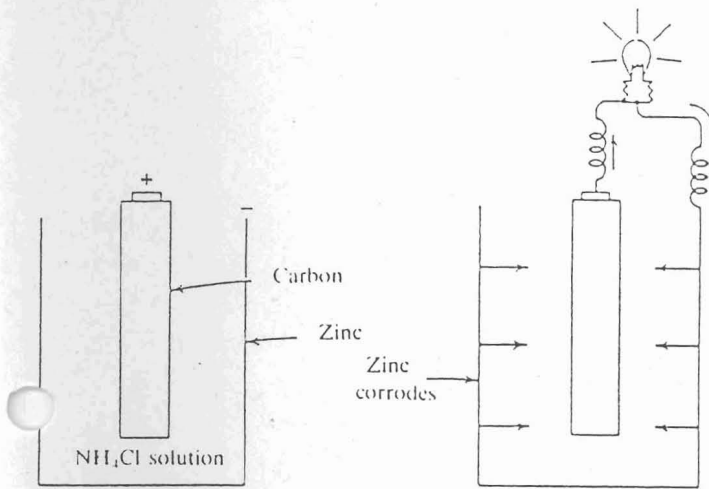


Fig. 1 Dry cell⁽¹⁾

As mentioned above, corrosion processes are chemical or electrochemical reaction. In aqueous media, the action is similar to that taking place in a cell made up of a center carbon electrode and a zinc cup electrode separated by an electrolyte consisting essentially of NH_4Cl solution (Fig. 1). At the carbon electrode (positive pole), chemical reduction occurs, and at the zinc electrode (negative pole) oxidation occurs, metallic zinc being converted into hydrated zinc ions. The greater the flow of electricity through the cell, greater is the amount of zinc that corrodes.

On an open circuit, zinc can corrode slowly. The slow consumption of zinc on an open circuit is accounted for largely by the activity of minute impurities, like iron, embedded in the surface of zinc. Any metal surface, similar to the situation for zinc, is a composite of electrodes electrically short-circuited through the body of metal itself (Fig. 2). So long as the metal remains dry, corrosion is not observed. But on exposure of the metal to water or moisture, local-action cells are formed and are accompanied by chemical conversion of the metal to corrosion products.

In the case of pure metal such as iron or steel exposed to the atmosphere, local-action cells are also set up when there are variations in the environment or in temperature. For iron or steel, the negative electrodes are commonly portions of the iron surface itself covered perhaps by porous rust (iron oxides), and positive electrodes are areas exposed to oxygen (Fig. 3). The amount of oxygen reaching the metal that is covered by rust is less than the amount that contacts other portions where permeable coating is thinner or absent. The positive and negative electrode areas interchange and shift from place to place as the corrosion reaction proceeds.

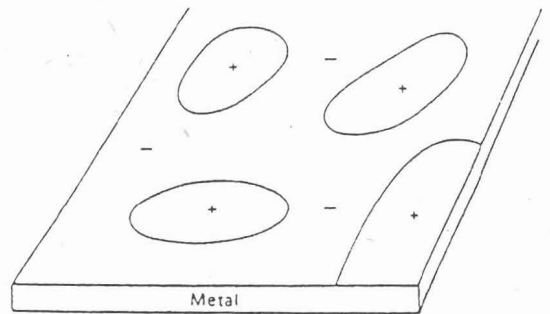


Fig. 2 Metal surface enlarged showing schematic arrangement of local-action cell¹

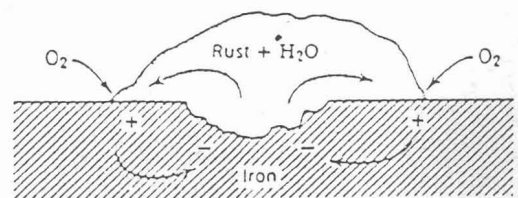
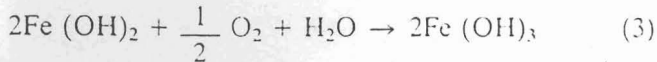


Fig. 3 Differential aeration cell formed by rust on iron¹

When there is water at the steel surface, the following reactions take place:



Ferrous hydroxide ($\text{Fe}(\text{OH})_2$) forms next to the steel surface. At the outer surface of the oxide film, ferrous hydroxide converts to ferric hydroxide by dissolving oxygen, in accord with



Ferric hydroxide takes place at the outer surface of the oxide film, and the corrosion reaction proceeds.

3. METHODS FOR PROTECTION OF STEEL MATERIALS AGAINST CORROSION

Since steel is not stable in nature, it tends to change to a stable form of oxide whenever it is exposed to atmosphere, water, or soil. Consequently in order to refrain from this behavior, proper protecting methods of steel against corrosion are required. These methods for protecting steel (exposed to atmospheres) against corrosion can be classified into five groups as follows:²

- Coatings (organic and inorganic)
- Metallic coatings
- Cathodic protection
- Alloying
- Control of environments

3.1 Coatings

Normally protective coatings applied to steel for protection against atmospheric corrosion are paints. Paints are mixtures of many raw materials. Some components can have a very significant effect when used in proportions as low as 0.01 per cent of the total, whereas others can be varied to some extent without having too drastic an effect. Basically, paint consists of three major components as follows:^{3, 5}

- Binder (sometimes called resin, vehicle, or polymer)
- Pigment and extender
- Solvent

Of these, only the first two form the paint film which protects and decorates the structures. The

solvent is present to give good application properties and is really an expensive waste material.

3.2 Metallic coatings

Metallic coatings are widely used in practice as an effective means for the corrosion control of metallic materials. Metallic coatings perform a long service life. It was reported that the service life of zinc coating, 400–700 g/m², may sometime be over 60 years.⁶ Metallic coatings can be divided into two classes, which is noble and sacrificial. For noble coatings (e.g. nickel, lead, silver, copper, or chromium) on steel, the direction of current accelerates attack of the base metal. But for sacrificial coatings (e.g. zinc, cadmium, or aluminum) on steel, the direction of current through the electrolyte is from coating to base metal; as a result of this, the base metal is cathodically protected (Fig. 4). So long as adequate current flows and the coating remains in electrical contact, corrosion of base metal does not occur.

The most common metallic coating used to protect steel in atmospheres is zinc coating. The main advantages of zinc coating are its long service life and its economic. Corrosion rate of galvanized steel plate is very low compared with mild steel (Table 1).⁷ There are also the other advantages as follows:⁸

- Good adhesive property
- Good surface finishing
- High reliability
- Can reduce time of construction

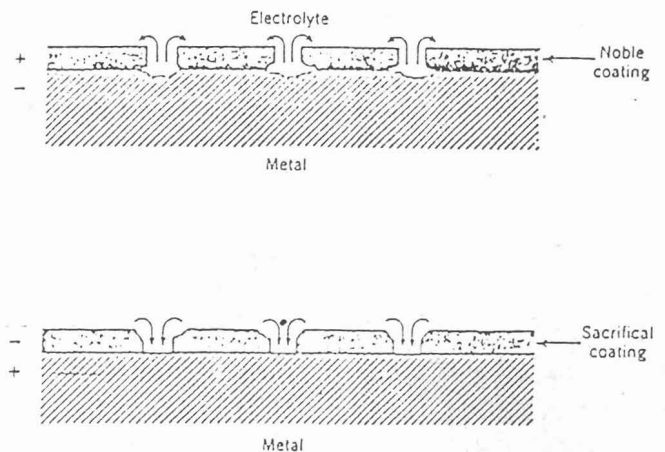


Fig. 4 Sketch of current flow at defects in noble and sacrificial coatings¹

Table 1 Corrosion rate of mild steel and galvanized steel in atmospheres (10^{-3} mm/y)⁷⁾

Environment	Japan			England		
	Place	Mild steel 0.06% C	Galvanized Steel 0.15% Al	Place	Mild steel 0.2% C	Galvanized Steel
Marine City	Oiso	40.5	1.28	Calshot	86.4	3.56
	Tokyo	61.2	1.52	Woolwich	101.6	3.81
Industrial Heavy Indus.	Kawasaki Industry	64.8	2.01	Motherwells	91.4	4.32
	Industry	116.0	7.78	Sheffield	139.7	13.20
Rural	Aizu	49.5	2.74	Llanwrtydells	66.0	2.79

3.3 Cathodic protection

In general, cathodic protection is useful for corrosion control of only submerged or buried metals that are exposed to aqueous environments or to media such as soils containing liquid electrolyte as the conducting component.^{9,10} Thus, it is frequently stated that the technique cannot be employed to prevent corrosion above the water line, because the impressed current cannot reach metal areas that are out of contact with the electrolyte.¹ However, Doufu¹¹ stated that cathodic protection can be employed with the combination of coating. The key to applying impressed current cathodic protection in atmospheric environments is to use a solid ionic conductor as an alternative to a liquid electrolyte, and the type of paint characterized by ionic conduction is required. Doufu found that the introduction of a solid electrolyte into the paint can solve this problem. The concept can be illustrated by Fig. 5.

The overall coating system is constructed by coating the metallic surface to be protected with the solid electrolyte containing coating (CK coating), then with an electronically conducting coating that acts as the anode. The metal is then cathodically polarized using an external dc source. To assist control of the cathodic potential, a graphite reference electrode is embedded in the CK coating.

By this method, steel materials can be protected against corrosion in atmospheres with high efficiency. Table 2 illustrates corrosion rates and protection efficiency under cathodic protection.¹¹

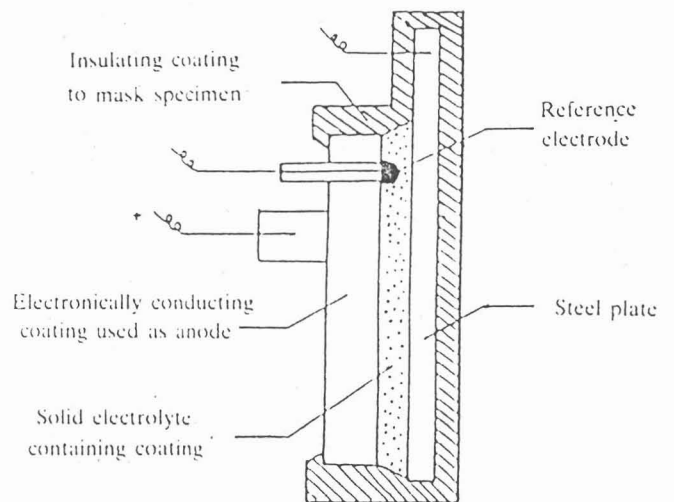


Fig. 5 Schematic diagram of electrode assembly used for experiments¹¹

3.4 Alloying

Alloying is an effective means for improving the resistance of metals to attack by corrosive environments. When alloyed with steel in small concentrations, copper, phosphorus, nickel, and chromium are particularly effective in reducing atmospheric corrosion. Table 3 shows the effect of low-alloy components on atmospheric corrosion of steel.¹

The usefulness of low-alloy steels to effectively resist atmospheric corrosion through formation of protective rust films has resulted in the development

of the so-called weathering steels. They are employed for construction of buildings or bridges without the

necessity of painting, thereby saving appreciable maintenance costs over the life of the structure.

Table 2 Summary of corrosion rates (by weight loss) and protection efficiency under cathodic protection by means of CK coating : 40°C, moist atmosphere, test duration 7 days¹¹

Condition	16 Mn steel		Mild steel	
	Corrosion rate (mm/year)	Protection efficiency (%)	Corrosion rate (mm/year)	Protection efficiency (%)
Control specimen without coating and cathodic protection	0.636	0	0.221	0
Coated specimen without cathodic protection	0.066-0.134	73.6-87.7	0.063-0.088	60.0-71.4
Coated specimen under cathodic protection*				
- 200 mV	0.027-0.073	88.5-95.8
- 350 mV	0.0078-0.0095	98.5-98.8
- 500 mV	0.0008-0.0045	99.3-99.9
- 700 mV	0.002-0.014	97.8-99.7
- 850 mV	0.016-0.036	93.3-96.9	0.0057-0.0060	97.3-97.4

* Voltages relative to graphite electrode

Table 3 Effect of low-alloy components on atmospheric corrosion of commercial steel sheet (Eight-year exposure)¹¹

Steel	Composition (%)				Loss of thickness	
	C	P	Cu	Other	(mm)	(mils)
Industrial atmosphere (Kearney, N.J.)						
Carbon	0.2	0.02	0.03		0.20	8.0
Copper-bearing	0.2	0.02	0.3		0.11	4.4
Low-chromium	0.09	0.2	0.4	1 Cr	0.048	1.9
Low-nickel	0.2	0.1	0.7	1.5 Ni	0.051	2.0
Temperate marine atmosphere* (Kurb Beach, N.C.)						
Carbon	0.2	0.02	0.03		0.24	9.5
Copper-bearing	0.2	0.01	0.2		0.15	5.8
Low-chromium	0.1	0.14	0.4	1 Cr	0.069	2.7
Low-nickel	0.1	0.1	0.7	1.5 Ni	0.076	3.0
Tropical marine atmosphere (Panama Canal zone)						
Carbon	0.25	0.08	0.02		0.52	20.4
Copper-bearing	0.2	0.004	0.24		0.45	17.6
Copper-chromium	0.07	0.008	0.1	3.2 Cr	0.23	9.1
Low-nickel	0.2	0.04	0.6	2.1 Ni	0.19	7.5

* 7.5-year exposure

3.5 Control of environment

The other method for protection of steel materials against corrosion in atmospheric environments is to control the environment. The methods of controlling humidity and removing impurities can be applied. As mentioned before, a critical humidity exists below which corrosion is negligible. Therefore, if humidity is controlled at lower than the critical value, corrosion protection will be effective.

Removing atmospheric impurities such as dust, sulfur-dioxide, and sea-salt particles is also effective for the protection of steel materials against corrosion. It was reported that if the atmosphere is thoroughly purified, there is no corrosion even at 99% RH.¹²⁾

4. CONCLUSION

The corrosion process of bare steel has been clarified in this paper. The methods for protecting steel materials that are exposed to atmospheres against corrosion were investigated. These protecting methods can be classified into five groups. They are coatings, metallic coatings, cathodic protection, alloyings, and control of environments.

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