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CORROSION MECHANISMS
IN THE DETERIORATION OF EXPOSED BRIDGE STEEL

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ABSTRACT

The total cost annually due to the effects of corrosion is estimated as high as \$126 billion dollars or by another estimate approximately 3 to 5% of the gross national product. This paper deals primarily with the thermodynamic reactions leading to the corrosion of steel, corrosion mechanisms and briefly on the systems for the protection of the metal surfaces. References are given which cover in great detail the work by others related to the deterioration of steel as well as other materials.

Next to pollution clean-up, the cost of maintenance and replacement of metal due to corrosion is probably a very close second. Figures of the cost due to corrosion vary widely from up to \$126 billion dollars per year or in another estimate about 3 to 5% of the gross national product of the various nations involved.

The battle against corrosion of structural and other members in bridges requires consistent maintenance and replacement after a certain time. Although these costs appear to be high, the cost associated with the liabilities of bridge collapse or major failures could be astronomical in comparison.

THERMODYNAMIC CORROSION MECHANISMS

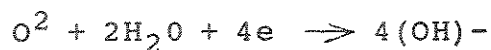
In nature there is a constant driving force ready to convert good steel back to the natural oxides. The free energy and other thermodynamic relationships show that the driving force is designed to change iron back into forms of iron oxide. In the manufacture of iron for steels the ore oxide is converted to pure iron only by the expenditure of much energy to reverse the cycle in nature. With due respect, one might relate this phenomena to the Biblical words, "from dust to dust".

Other metals such as zinc in galvanizing undergo the transformation to the oxide form at rates depending on the metal.

Various cathodic reactions are encountered in metallic corrosion systems and include as follows:

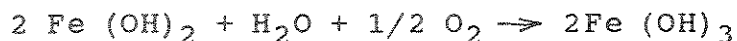
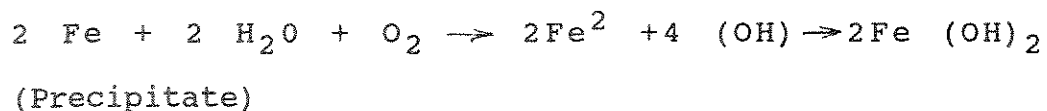
- 1) Hydrogen Evolution
 $2H + 2e \rightarrow H_2$
- 2) Oxygen Reduction
 $O_2 + 4H + 4e \rightarrow 2H_2O$
- 3) Oxygenation-Reduction (neutral or basic)
 $O_2 + 2H_2O + 4e \rightarrow 4(OH)^-$
- 4) Metal Ion Reduction
 $M_3^+ + e \rightarrow M_2^+$
- 5) Metal Deposition
 $M^+ + e \rightarrow M$

When coated steel (iron) is in contact with water or seawater corrosion will be expected if the environment makes actual contact with the steel by penetration of the coating. Since water and seawater are almost neutral the cathodic reaction as previously shown is:



Sodium and chlorine ions in the water do not actually participate on a one to one basis in the reaction.

The overall reaction from combining the above reaction with the reaction of the iron becomes:



When the final product is dry it becomes $\text{Fe}_2 \text{O}_3$, the rust form of iron hydroxide.

If the surface of the metal is coated with paint or non-conducting film the rate of the anodic and cathodic reactions will be greatly reduced and as a result corrosion would be retarded. However, it is well known that no coating system is perfect and that pin holes, holidays or other deficiencies would allow in time increasing contact of the environment with the steel underneath.

COATING BREAKDOWN

Most coatings permit moisture and oxygen to permeate the system and to attack the steel. The various degrees of attack would include:

- 1) Blistering or rust spotting. The degree of this condition can be determined by reference to the Steel Structures Painting Council (SSPC) or the ASTM D610.
- 2) General rusting
- 3) Coating disbonding
- 4) Pitting and flaking
- 5) Structural loss

It is interesting to note that certain alloy steels such as weathering steels are specially compounded to develop a patina or corrosion layer. This subject is covered in detail in some of the references attached (1, 2, 3).

COATING SYSTEMS

In general, there are three types of coating systems. The most familiar system would be paint as a barrier against the environment. This could involve a wide range of heavy mastic coatings to complex combinations of various paint layers applied to the steel. Proper surface preparation in accordance with the SSPC requirements is the most important stage in the application of a protective system to metal.

A somewhat different type of coating system would include the partial passivation of the steel by the presence of slightly soluble inhibitors in pigments such as chromates, phosphates, silicates, plumbates and borates.

A third type of coating system for the protection of steel would be the use of a sacrificial or galvanic protection coating such as organic or inorganic zinc.

A more drastic system for the protection of steel structure would be the use of cathodic protection directly connected to the coated steel. The selection of sacrificial anodes or impressed current would depend on the size and geometry of the structure and location.

CORROSION MECHANISMS

The following is a brief summary of the various corrosion mechanisms which could be at work on bridge steel:

1) General

- A) General corrosion is defined as a condition that more or less uniformly exists on a surface undergoing corrosion.

2) Localized

- A) Pitting in which the diameter of the localized corrosion is less or the same as the depth of the corrosion and is probably related to oxygen corrosion cells.

Crevice

- B) A special kind of pitting which occurs primarily in stagnant zones with the anode part of the metals depending on the oxide films for passive layers.

3) Galvanic

- A) Corrosion related to the reaction between dissimilar metals. The electromotive table classifies the anodic or cathodic position of the metal with regard to any other metal in the table. In general, if the metal is above iron (steel) that metal would be sacrificial, anodic and should protect the steel. However, special considerations such as relative sizes and environment may change the expected result.

Galvanic corrosion potential could exist between the mill scale and the steel in bridge structure.

The mill scale being more cathodic would cause the corrosion of the steel.

4) Stray Current

A) Stray current can be harmful to structure depending on the direction of the stray current. If the stray current is returning back to its source through another member, it is very likely that this member will become anodic and be "corroded". It is very important to determine the presence of strong current by copper/copper sulfate determinations.

5) Erosion and Erosion Corrosion

A) Erosion and erosion corrosion are based on the movement of fluids across the metal surfaces. This movement could remove the protective oxide or initial end product thus exposing fresh new surfaces for attack. This would be the case in the splash zones of movable bridges where the action of the fresh or salt water would be removing the protective layer.

6) Cavitation

A) Cavitation is a special kind of erosion corrosion and as is related to a much higher velocity in the water impinging against the metal.

7) Fretting

- A) The fretting or rubbing between mating surfaces of metals will in effect remove protective formations and expose fresh metal to more rapid corrosion.

STRESS ASSISTED CORROSION

There are several modes of corrosion assisted by stress. These combinations are identified below.

INTERGRANULAR CORROSION

Intergranular corrosion is the corrosion which occurs around the grain boundaries. This condition can arise because of the electromotive differences between the composition of the grain and the grain boundaries.

CORROSION FATIGUE

When the combined action of fatigue stresses and corrosion exists the speed of the corrosion process is generally accelerated. In fatigue, even without corrosion, failures can occur at a fraction of the yield strength. The sharp intrusions of cracks and/or corrosion spikes act as stress risers.

STRESS CORROSION

This type of corrosion deals with the presence of static stresses with corrosion attack. Stress concentration problems are also applicable.

We have seen that many chemical mechanisms in nature exist for the natural conversion of the structural steel in movable or stationary bridges back to the powder form of the original ore which has no strength. The environment of salt air, constant wetting and drying, condensations, erosion, abrasion, fatigue and static stresses with corrosion will shorten considerably the life of the bridge structures unless strict measures are adopted to properly apply the state of the art protection system and to maintain the system by regular inspection and repair as required.

In the field of corrosion we must recognize the fine work of the NACE, ASME, ASTM, ASM and other technical and scientific organizations and many individuals such as Frank Laque and Mars Fontana for invaluable contributions by their studies of corrosion and determining ways and means to cope with the problems.

I appreciate the opportunity of presenting this paper to you as attending members of the Second Biennial Movable Bridge Symposium sponsored by the American Society of Mechanical Engineers in cooperation and conjunction with Florida Department of Transportation.

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