



ISSN: 2456-799X, Vol.03, No.(2) 2018, Pg. 68-74

## Oriental Journal of Physical Sciences

www.orientjphysicalsciences.org

### Corrosion- Yesterday, Today and Tomorrow

SUSAI RAJENDRAN

Department of Chemistry, St. Antony's College of Arts and Sciences for Women  
Thamaraipadi Dindigul, Tamil Nadu- 624 005 India.



#### Article History

Published on 25-December-2018

In the olden days , at the dawn of history, native metals were used. During this period corrosion problem was not there. With the beginning of use of iron, the problem of corrosion started. Rusting of iron was noticed.

Corrosion is the deterioration of material when it comes in contact with environment. Corrosion is a spontaneous process; a natural process; a thermodynamically favourable process. Corrosion is considered as the expression of desire of the metal to go back to its original state of ore. Man is made of ashes. He will go back to ashes. Corrosion is like death. It is sure and certain. We are born to die? No! We are born to live; to live happily and making other also happy. However death is unavoidable just like corrosion. We can postpone death. We cannot prevent it. Similarly we can control the rate of corrosion process. We cannot prevent corrosion. This is the philosophy we derive from the history of process of corrosion.

#### Corrosion - An Electrochemical Process

The first thought of electrochemical nature of corrosion process originated when Austin in 1788 noticed that neutral water became alkaline when metal reacted with water. He proposed that it was due to ammonia. But later it was proved to be due to sodium hydroxide. It was the product of cathodic reaction.

In 1819, A French writer (Thenard ) proposed that corrosion was an electrochemical process.

de la Rive in 1830 noticed that the attack of acid on impure zinc was more severe than on pure zinc.

During 1834-1840, Researches of Faraday revealed that electric current was produced by chemical reactions. He provided a quantitative relation between the two.

**CONTACT** Susai Rajendran ✉ [susairajendran@gmail.com](mailto:susairajendran@gmail.com) 📍 Department of Chemistry, St. Antony's College of Arts and Sciences for Women Thamaraipadi Dindigul, Tamil Nadu- 624 005 India.



© 2018 The Author(s). Published by Exclusive Research Publishers

This is an Open Access article licensed under a Creative Commons license: Attribution 4.0 International (CC-BY).

**Passivity**

Faraday proposed the concept of passivity. In 1836, Schonbein (Professor of Chemistry, at Swiss University of Bale) contributed more in the field of passivity. That is a strange inactive condition of iron was observed. This was favoured by anodic action. It should be noted that normally anodic reaction favours corrosion and cathodic reaction prevents corrosion.

**Contribution of Ostwald and Nernst for the Electrochemical Nature of Corrosion**

After the period of Faraday the electrochemical nature of corrosion could not be established because, the available knowledge on electrochemistry was not sufficient to explain the electrochemical nature of corrosion. However, the concept development on single electrode potential by Ostwald and Nernst paved way for the electrochemical nature of corrosion.

In 1900, Wilsmore published an important paper. In Great Britain, it was proposed that corrosion was due to presence of certain substances or due to formation of substance on the metal surface. This was consistent with electrochemical nature of corrosion.

**Role of Acids in Corrosion Process**

During 1888-1908, it was thought that corrosion was mainly due to the attack of metals by acids. It was proposed that Carbonic acid was responsible for rusting of iron.

Dunstan, Jowett and Goulding (1905) proposed that rusting of iron took place in presence of water and oxygen. This could take place even in the absence of carbon dioxide (an acidic gas).

In 1908, Tilden, Heyn and Bauer supported this view experimentally. Acid was not necessary to rust iron. Salt solution was needed to corrode iron. During the corrosion process the salt solution became alkaline. Interestingly it was observed that during corrosion process, hydrogen gas was liberated. This evolution was observed more rapidly in acid medium than in neutral medium. In atmospheric corrosion process also, if acidic gases were present in the air, evolution of hydrogen was noticed.

In 1935, Vernon proved experimentally that sulphurous acid was responsible for atmospheric corrosion and not carbonic acid. He proved that carbon dioxide could prevent the attack on iron.

**Formation of Hydrogen Peroxide during Corrosion Process**

In 1900, presence of hydrogen peroxide was detected during corrosion of metals. It was thought to be an intermediate product during corrosion process. This product can occur if, during corrosion process, there is access of oxygen in the cathode region.

**Evolution of Hydrogen Gas- An Evidence for Electrochemical Nature of Corrosion**

In 1901, Scientists working in Arrhenius laboratory namely Ericson-Auren and Palmaer, proposed that liberation of hydrogen by action of acids on metals, was a strong evidence for electrochemical nature of corrosion. During this process there was formation of microscopic cells, which they called "local elements". Similar views were expressed by American Scientists Whitney (1903) and Cushman (1907), working on neutral liquids.

**Role of oxygen in Corrosion Process**

During 1907- 1908, there was dispute over the role of oxygen in the process of corrosion. Some scientists overlooked the role of oxygen in corrosion process. Some scientists recognized the role of oxygen as cathodic stimulator.

American scientists Corey and Finnegan (1939) and de Kay Thompson (1940), suggested that iron is slowly attacked by oxygen-free water, with liberation of hydrogen. Interestingly, in this case the final product is not yellow rust (ferric hydroxide) but black granular magnetite or sometimes ferrous hydroxide.

#### **Corrosion Rate and Galvanic Corrosion**

During 1908-1910, German scientists Heyn and Bauer they calculated velocity of corrosion reactions of iron and steel. The velocity was calculated in different liquids in different conditions. The corrosion rates were measured for individual metals and also in presence of other metals.

During these studies it was observed that when iron was in contact with nobler metal, the corrosion of iron was accelerated. But when iron was in contact with a baser metal, the latter underwent corrosion while iron was protected from corrosion.

Whitman and Russell, in 1924 proved that corrosion rate may increase when anodic area is small and cathodic area was large. This view was supported by the works of Akimow, Clark and others, published in Russia (1935).

In 1923, It was noticed that if dissimilar metals are in contact through an electrolyte, "galvanic currents" would be set up.

These concepts later were proved to be that of galvanic corrosion and cathodic protection.

#### **Cathodic protection**

The idea of galvanic corrosion prompted Sir Humphrey Davy to propose that to protect copper in seawater, copper may be connected with iron or zinc. In this case copper will be protected and iron or zinc will undergo corrosion. Again this is the concept of galvanic corrosion or cathodic protection.

#### **Differential Aeration Corrosion**

In 1931, the German scientist, Tammann pointed out that electric currents can arise if the metallic surface is wetted by liquid having differences in oxygen content.

The Italian scientist, Marianini, in 1830, proposed that variations in oxygen concentration can set up electric currents. This view was supported by the works of the German, Warburg (1889), and the Russian, Kistiakowsky (1908).

In 1916 The American, scientist Aston proposed that local differences in oxygen concentration promoted the rusting of iron.

The American scientist McKay in 1922 showed that currents could also be set up on a single metal by variations of metal ion concentration in the liquid.

During 1923, The importance of "differential aeration currents" was realized. This was due to difference in oxygen concentration.

The electric currents flowing over the surface of metal corroding in salt solutions were detected and measured by several researchers including Bannister, Hoar, Thornhill, Agar, Mears and Brown (1931-1939).

#### **Conclusion from Studies on the Corrosion of Salts and Acid**

Thus studies on the corrosion of salts and acid led to the conclusion that corrosion of metals is of electrochemical in nature. The electrons flow from anodic to cathodic areas present in different parts of the

metal. The products of the anodic reaction and cathodic reaction combine to form a sparingly soluble end product such as rust, as in the case of iron.

### **Inhibitors**

It is possible to control the anodic and cathodic reactions by coating with sparingly soluble compounds such as anodic inhibitors and cathodic inhibitors.

In 1938, the Polish investigator, Chyzewski classified the inhibitors into two groups namely anodic inhibitors and cathodic inhibitors. The anodic inhibitors are more effective and more dangerous; more dangerous in the sense that corrosion will be severe if the concentration of the anodic inhibitor exceeds the optimal level. In the work published in America by Cushman and Gardner (1910) pointed out that many substances used as pigments in paints behave as inhibitors. Zinc rich paints improve the corrosion resistant property of paints.

### **Iron Oxide- Rust**

Forrest, Roetheli and Brown (1930-1931), showed that rust coats varied in protective character according to the rate of supply of oxygen to the surface.

Several investigators proposed that oxides of iron can in effect act as oxygen-carriers.

In 1921, Friend suggested that a colloidal solution of ferric hydroxide behaves as a carrier for oxygen, passing alternately between the ferrous and ferric conditions.

Later (1936-38) Herzog attributed a rather similar role to "solid" rust, but combined this with an electrochemical mechanism.

After long immersion in stagnant water, iron frequently becomes covered with an inner layer of magnetite, overlaid with an outer layer of ferric hydroxide. The magnetite is supposed to act as cathode towards the iron as anode, and the ferric hydroxide just above suffers cathodic reduction to hydrated magnetite. This may either lose water, reinforcing the magnetite, or may absorb oxygen from the air, returning to the state of ferric hydroxide.

### **Passivity**

During 1927, many scientists concentrated on the electrochemical study of passivity. They insisted that the experiments on passivity should not be of a short period but of a long period as in the real process of passivity. In this connection, the contributions of scientists like W. J. Muller, Konopicky, Machu, Bengough, Stuart, Lee and Wormwell.

### **High Temperature Oxidation**

Whilst the mechanism of low-temperature corrosion was being investigated, high-temperature oxidation was also under study and here it was found possible to establish simple laws of growth.

The scientific study of the oxidation process may be said to have begun with the classical work of Pilling and Bedworth (1923).

Pfeil (1929-31) showed that the growth of oxide consisted in the movement of metal outwards rather than the penetration of oxygen inwards through the scale.

In 1934, the German physical chemist, Wagner, showed that high-temperature oxidation is connected with the passage of cations and electrons outward through the growing scale; low-temperature tarnishing, due to sulphur compounds in the air, follows a similar mechanism. A mathematical relationship was established

between the oxidation rate and the electrical properties of the film substance; this shows that good resistance to oxidation may generally be expected where the electrical resistance of the oxide formed is high.

#### **A New and Instructive Derivation of Wagner's Equation**

In 1938, a new and instructive derivation of Wagner's equation was published by Hoar and Price.

Price and Thomas, applied these new theoretical ideas to the development of a process known as selective oxidation, which produces enhanced resistance of copper alloys to high-temperature oxidation.

#### **Examination of the Oxide Films**

This was done with x-ray diffraction technique and by ellipsometry.

Films which produce interference tints on the metal usually display complementary colours after transfer to transparent plastic.

A form of film-stripping suitable for the chemical estimation of the constituents was developed by Vernon, Wormwell and Nurse in 1939.

#### **Atmospheric Corrosion**

From 1923 onwards Vernon published several research papers related to studies of the behaviour of metals exposed to the atmosphere. This study established simple laws connecting corrosion and time. One of the important results attributable to Vernon, Hudson and Patterson was the Principle of Critical Humidity; it was found that frequently corrosion only became rapid in air when the humidity exceeded a certain value. Hudson's (1929-45) extensive researches have established the relative resistance of different materials in numerous different atmospheric conditions, and in the case of iron and steel have indicated how best protection can be achieved by coatings of paint or non-ferrous metal.

#### **Corrosion during Time of the War of 1914-18 and 1935-1945**

This period is considered as the period of war. During this period Pure Scientists carried out experiments on corrosion.

The work on the corrosion of condenser tubes attracted many researchers including Corrosion Committee of the Institute of Metals. The experimental work was carried out in the early years by Bengough and several colleagues. Largely as a result of the work of Bengough, May, and their colleagues, along with the industrial development of new corrosion-resisting alloys, the position so much improved that in the war of 1939-45, condenser trouble, although not unknown, caused little anxiety.

#### **Corrosion Studies in Various Countries**

Various countries were interested in solving their own corrosion problems.

For example, marine corrosion has been extensively investigated in Great Britain while corrosion troubles in hydroelectric installations have received attention in Switzerland and Northern Italy.

The bacterial attack upon pipes buried in clay soils was first studied in detail by the Dutch bacteriologist, von Wolzogen Kuhr, while special methods of protecting long pipe-lines have been worked out in the United States.

#### **Corrosion Problems in Industries**

Instead of studying pure corrosion, corrosion problems in various industries attracted the attention of corrosion scientists. Corrosion due to chemical and mechanical stress, and intergranular cracking were studied. Moore and Beckinsale in 1920-1923 extensively studied on intergranular cracking.

In view of the development of aircraft, very important thing is the stress-corrosion cracking of certain aluminium alloys. The views held to-day owe much to the Russian investigator, Akimow, the American group associated with Dix, the British group led by Sutton, the Swiss metallurgists, von Zeerleder and Bosshard, and the German investigator, Bollenrath.

### **Corrosion –Fatigue**

This is a dangerous form of corrosion. the combination of alternating stress and corrosio. It involves the combination of alternating stress and corrosion. This was observed during the war of 1914-18 on paravane towing ropes. Haigh was the first to ascribe their rapid failure to conjoint chemical-mechanical action. Around 1926 the American investigator, McAdam, commenced an extensive set of elaborate tests on corrosion-fatigue. His earlier results were brought into a convenient compass by Gough in a lecture delivered in 1932.

### **Mechanism of Corrosion**

During the past three decades attention is paid to mechanism of corrosion and its control. Although the kinetics of such reactions are in many cases well established, and obey relatively simple laws for which a logical interpretation can usually be provided, it is a strange fact that to-day such laws receive no attention in most textbooks of chemical kinetics, and often remain unmentioned in lectures on physical chemistry given to students. It is interesting to note that the velocity of a reaction often diminishes as temperature rises.

### **Thermodynamics of Corrosion**

An important aspect is the thermodynamics of corrosion.

Many corrosion reactions-thermodynamically possible-do not in practice occur because the corrosion product stifles them by isolating the reactants. Nevertheless, Thermodynamics, applied to corrosion by those who are masters in both fields, can yield most fruitful results, as shown by the work of Gatty and Spoonerand of Warner, and recently by that of the Belgian, Pourbaix.

### **It is Time to Think**

Corrosion problem is insidious. It is invisible and invincible . We feel it only when we see the results of it. Many problems of corrosion , the theories and methods of prevention/ control of corrosion are not found in a single book. The knowledge of these aspects should be included in text books of schools and colleges and universities. In Governments separate ministry should be formed to deal with these issues because many accidents in ships, planes and trains and bridge accidents are mainly due to corrosion failures.

### **It is Time to Act**

Corrosion costs us an astounding US 2.5 trillion dollars globally. However, with the available knowledge 50% of the corrosion problems can be solved. To make it 75%, many measures have to be taken up. It is right time to introduce corrosion studies in Educational institutions starting from schools to Universities. It is high time for World Corrosion Organisation to make this mandatory throughout the world. To this effect a resolution may be adopted in UNO. Corrosion Awareness Day may be celebrated on April 14 in Educational Institutions and Industries throughout the world. Corrosion auditing and management is essential periodically, in various industries, bridges, equipments and historically important monuments. The metal rods used for windows may avoid designs bends, architects and weld. This will avoid corrosion. It is very interesting to note that in India many corrosion conferences are conducted by NACE International- India section, NCCI having base at CECRI, Karaikudi, India and Electrochemical Society of India, having base at Bangaluru, India. One cannot forget the contributions of EUROCORR, organized every year in various parts of the world.

### References

1. Uhlig HH. The Cost of Corrosion in the United States. *Chemical and Engineering News* 1949; 27: 2764.
2. Koch, G. H, Brongers, M. P. H., Thompson, N. G., Virmani, Y. P., and Payer, J. H. Corrosion Costs and Preventive Strategies in the United States. FHWA-RD-01-156. 2001. Springfield, VA, National Technical Information Service.
3. Economics of Corrosion. NACE 3C194. 1994. Houston, TX, NACE International.
4. Roberge PR. *Handbook of Corrosion Engineering*. New York, NY: McGraw-Hill, 2000.
5. Roberge PR. *Corrosion Basics - An Introduction*. 2nd edn. Houston, TX: NACE International, 2006.
6. Henthorne M. Materials Selection for Corrosion Control. *Chemical Engineering* 1971; 1139-146.
7. *Corrosion Data Survey Metals*. 6th Edition edn. Houston, TX: National Association of Corrosion Engineers, 1985.
8. *Corrosion Data Survey Non-Metals*. 5th Edition edn. Houston, TX: National Association of Corrosion Engineers, 1975.
9. Gundry RD. Corrosion/93 Plenary & Keynote Lectures. Houston, TX: NACE International, 1993.
10. Lynes W. Some Historical Developments Relating to Corrosion. *Journal of the Electrochemical Society* 1951; 98: 3C-10C.
11. <https://corrosion-doctors.org/Corrosion-History/Timeline.htm>
12. <https://corrosion-doctors.org/Corrosion-History/Theories.htm>
13. <https://corrosion-doctors.org/Why-Study/Historical-perspective.htm>