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A REVIEW OF THE CORROSION BEHAVIOR OF METALLIC HERITAGE STRUCTURES AND ARTIFACTS

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Graphical abstract

Zinc corrosion in sculpture

Abstract

Awareness about restoring and preserving historically important structures and artifacts is gradually growing in many parts of the world. These artifacts and structures represent the culture, tradition and past of a nation. They are often also a source of national income through tourist activities. Besides masonry and wood work, metallic forms and relics are a vital part of the heritage which needs to be conserved. Certain metals have been used significantly throughout history in the creation of objects and structures. However, metals are prone to decay over time, particularly decay through corrosion. The basic mechanisms of metal corrosion, the various types of corrosion and existing remedial solutions are reviewed in this paper. The most significant factor affecting metal corrosion was found to be the surrounding environment, especially in marine areas. Different remedial measures can be implemented on corroded metals according to their specific properties. Recommendations for further study are offered at the end of the paper.

Keywords: Corrosion, heritage structure, metal; artifacts, decay

Abstrak

Kesedaran mengenai mengelokkan dan mengekalkan bangunan bersejarah dan artifak sedang berkembang di seluruh dunia. Artifak dan bangunan ini melambangkan budaya, tradisi dan sejarah sesebuah negara Ia juga sering mengumbang kepada sumber pendapatan negara melalui aktiviti pelancongan. Selain batu dan kayu, besi juga telah digunakan dengan banyak di sepanjang sejarah penciptaan objek dan struktur. Namun, besi sering mengalami pereputan semakin masa berjalan, terutamanya pereputan melalui karat. Mekanisma asas bagi karat besi, jenis-jenis karat dan cara pemulihan sedia ada telah dikaji dalam kertas kerja ini. Faktor paling penting bagi karat besi didapati adalah keadaan persekitaran, terutamanya di kawasan marin. Pelbagai jenis teknik pemulihan boleh dijalankan ke atas besi berkarat mengikut sifat-sifat tertentu besi tersebut. Cadangan bagi kajian lanjut ada diberikan di penghujung kertas kerja ini.

Kata kunci: Kakisan, struktur warisan, logam, artifak, pereputan

1.0 INTRODUCTION

Historic structures and artifacts are icons of the culture and customs of a nation. The heritage of a nation is composed of tangible and intangible components such as architecture, art, history, archaeology, as well as financial, social, political and religious or symbolic practices and beliefs. Intangible heritage in the form of professional craft knowledge is materialized in historic objects as part of their intrinsic and sometimes hidden and indiscernible value [1, 2]. According to B. M. Feilden "a historic building is one that gives us a sense of wonder and makes us want to know more about the people and the culture that produced it". He stresses the emotional value and symbolism of cultural identity and continuity, and qualifies a building as "historic".

Interest in conserving historic structures and artifacts is steadily increasing in many parts of the world [3]. Conservation is the action taken to prevent decay and manage changes dynamically. It embraces all acts that prolong the life of cultural and natural heritage. The actions taken should be reversible and not prejudice possible future interventions. The scope of conservation in built environments is ranged from territorial planning to the preservation or consolidation of a crumbling artifact.

Tangible and intangible heritage have become a source of income generation for many countries by attracting people from other nations. According to House of Commons (2004), heritage structures can act as income generation sources by attracting tourists from around the globe. Most studies in this field have concentrated on masonry structures, although a significant number of metallic structures have also received attention [4-6]. In different civilizations metals were used for different purposes, such as for structures, artifacts and weapons [7]. As these metallic heritages have aged, they have deteriorated and become corroded. Primary pollutants such as SO_2, NO_x, and CO_2, under the influence of O_2, humidity, sunlight, and temperature react to form new secondary pollutants [5, 8].

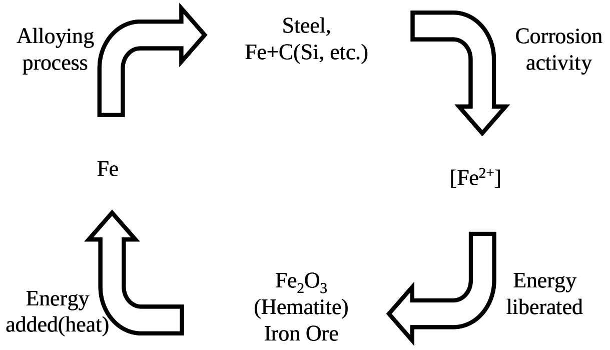


Figure 1 Refining-corrosion cycle

The deterioration of metallic structures is mainly due to corrosion, a natural process which has existed since man first began to make and use metals [6, 9, 10]. This process is a chemical reaction between metal and other substances. The most common reagents are oxygen and water. A layer of oxide forms on the surface in this reaction. In some metals, if this layer is dense and hard, it can be protective [11].

Corrosion is also affected by the position of metals in the electrochemical series: Au > Ag > Cu > Sb > Sn > Pb > Ni > Co > Cr > Fe > Zn > Mn > Al – Mg. Resistance to corrosion is determined by the position of the metal in the electrochemical series, in which metals are arranged by their electrical potential. Any metal in the above series is electronegative to all the metals which precede it and electro-positive to all that come after it. The process of corrosion is actually part of the cyclic nature of extractive metallurgy. For example, as shown in Figure 1, iron is manufactured from hematite by heating it with carbon but gradually oxidizes and degenerates into rust as it follows its natural life cycle [12, 13]. Hematite and rust are similar in composition.

Historic places and structures are symbols of a country's culture and memorials of its past and deserve to be preserved in their own right. However, for most historic places and structures the main source of income is from tourists. In order to attract tourists, these heritage sites have to be protected and preserved from damage and destruction. This paper presents an extensive review of the corrosion process of historic metal structures and artifacts. The aim of this paper is to present a basic understanding of the corrosion process of heritage metallic forms, which may be helpful to engineers, stakeholders and restoration workers. The first segment of this paper discusses the basic mechanisms of metallic corrosion and the subsequent part discusses remedial techniques and their procedural implementation.

2.0 HISTORICAL METAL USE

Metals have been used by man for thousands of years. The earliest communities and civilizations mainly used metals to make weapons and tools. They explored the use of metals and how to enhance the efficiency of metals to prepare quality weapons.

- Copper and one of its frequently used alloys, bronze (90% Cu, 10% Sn), have been used since ancient civilization. From historical evidence, it has been found that copper and bronze have been in use from at least 7000 BC.
- Iron, in different forms such as wrought iron, cast iron and steel, have been used since 4000 BC.
- Zinc was first used during the 18th century.

Besides copper, iron and zinc, other metals such as lead (Pb) and various alloys like brass (60% Cu, 40% Zn) and nickel (65% Ni, 30% Cu) were used for different purposes [14]. Tin (Sn) was occasionally used for sculptures with Zinc (Zn) painted on the sculptures as a protective coating.

3.0 CONSIDERATIONS FOR HISTORICAL METAL RESEARCH

Table 1 outlines several points that must be assessed before proceeding with any research or repairing of metallic heritage structures or objects.

Table 1 Parameters to evaluate usage and deterioration of heritage metal

Research	Parameters	Items to consider
Understand the structure or object	How does the object or structure work	Construction details Effect resulting from function (e.g. fountain)
Integrity	Visible stress fractures External influences	Drainage, subsidence, impact damage, stress fractures
Fixings	Identify fixing materials	Condition Structural integrity
Materials	Identify materials used	Cast iron/wrought iron/mild steel Other materials Combinations of materials
Corrosion	Intensity Range	Uniform, localized Analysis of corrosion products
Coatings	Sample	Stratigraphy Record sample locations Gilding
Previous repairs	Identify Assess	-
Recording	Photography Drawn survey Report	-

4.0 ATTRIBUTES OF HISTORICAL METALS

Conventional usage of metals can be classified into two categories: Ferrous (containing iron) and non-ferrous (containing no appreciable portion of iron). Generally, non-ferrous metal objects are more corrosion resistant. The general properties of metals that need to be taken into consideration are density, malleability, elasticity, ultimate tensile strength (tenacity), coefficient of linear expansion, thermal conductivity and specific heat.

4.1 Iron

Iron is a dark gray metal. The pure form of iron has been found in meteorites that have crashed into earth from outer space. Volcanic eruptions over millions of years have deposited iron in the form of iron ore (rocks with varying percentages of iron). Different civilizations have attempted to extract iron from ore with different success rates. Historically, the Romans improved iron extraction technology and produced better armor. The advent of the industrial revolution led to a better understanding of the iron manufacturing process and iron become more widely used [15, 16]. Different forms of iron have been used over time. They are, in order of appearance, wrought iron, cast iron, mild steel and recently stainless steel. Figure 2 shows various exposed structural steel samples with different levels of corrosion severity.

Figure 2 The unequal corrosion of different structural steels

4.1.1 Wrought Iron

Early forms of wrought iron were also called ‘charcoal iron’. Wrought iron was generally manufactured through a method called ‘direct reduction’. Iron ore (iron oxide with various impurities) was smelted by heating it with charcoal in small furnaces called 'bloomeries'. In this chemical process, carbon monoxide is released as the charcoal diminishes the iron oxide to iron.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \qquad (1)$$

Wrought iron is considered pure iron with a small amount of carbon (less than 0.15%) and usually a little slag. The mechanical strength of wrought iron is low. Improvements in ductility and tensile strength can be made by re-heating and re-working. It is soft and malleable, but can be toughened and made fatigue resistant. It has some resistance to corrosion. Up until the 14th century, wrought iron was mainly used for spears, swords and knives. Structurally, its use was restricted to tie bars. Starting from the 18th century, this metal was also used for beams and girders.


(a)

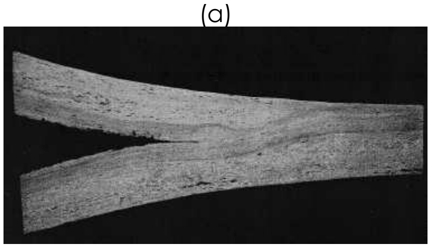

(b)

Figure 3 Examples of wrought iron [17]

Wrought iron objects were used in ancient civilization [18]. The Romans commonly used wrought iron doors. Its structural use dates from the Middle Ages when wrought iron bars were occasionally employed as tie bars for masonry arches and domes. Due to its superior tensile capacity, usage of wrought iron dominated the canal and railway ages, as cast iron is strong only in compression [9, 11]. A fractured wrought iron bar in Figure 3 shows the fibrous structure which makes wrought iron ideal for working under the hammer [17].

4.1.2 Cast Iron

Cast iron is considered an alloy. Its high carbon content (1.7% to 3.7%) gives it a better corrosion resistance capacity than wrought iron or steel [12, 19]. Variable amounts of silicon, sulfur, manganese, and phosphorus are also present in this alloy. Different techniques and compositions used during melting, casting and heat treating influence the characteristics of the final cast iron product.

Figure 4 Cast iron steps with highly decorative patterns

Various decorative and structural forms can be produced from molten cast iron [20]. The properties of cast iron are quite different from steel and wrought iron. Cast iron is too hard and fragile to be shaped by hammering, rolling, or pressing. It possesses greater compressive capacity, though weak in carrying tensile loads. Unlike the other forms of iron, it can withstand buckling loads with more rigidity. However, its inferior tensile capacity is disadvantageous as there is no warning before failure.

As cast iron is able to carry high compressive loads, mainly compression members like columns, struts and staircases were made from it (Figure 4). Cast iron often contains mold lines, flashing, casting flaws, and air holes. However, cast iron elements are very uniform in appearance and are frequently used repetitively. Cast iron elements are often bolted or screwed together [21].

Table 2 The effect of corrosive agents on bronze

Agent	Salt formed	Color of patina
Oxygen	Oxide	Red brown to dark black
Oxygen and chlorine	Chloride/Oxychloride	Very pale green
Carbonic acid	Carbonate	Green
Sulphuric acid	Sulphate/Basic Sulphate	Deep blue/Green
Nitric acid	Nitrate	Blue green to blue
Sulphur	Sulphide	Dark brown or black

Cast iron is vulnerable to a specific kind of corrosion, called graphitization, where porous graphite is impregnated with insoluble products. Graphite and iron silicon act as electrodes and dissolve the iron matrix. The cast iron objects preserves their appearance and profile, but are structurally weakened. This phenomenon generally happens when cast iron products are not painted for a long duration, when joints fail and acidic rainwater corrodes pieces from the exposed side.

4.2 Copper

Copper is widely used for architectural purposes as it has a high corrosion resistance capacity. The commonly used copper alloys are:

- Brass – Copper is alloyed with zinc (Zn) with copper varying from 90-60%, which affects properties and color of the metal. Sometimes magnesium and aluminum are also added.
- Muntz metal – Around 60% copper and 40% Zinc is used to make Muntz metal. This alloy is

generally used for decorative tiles, sheets and plainer surfaces.

Copper develops a patina by weathering. Especially in roofing the patina can vary depending on exposure. Usually, it will first become a coppery red, gradually deepening to a dark brown. In lighter corrosive environments, a green patina may develop in the form of copper carbonate. In highly polluted environments, the patina may change from blue to black. Severe corrosion attacks of copper roofs are caused by acidified rainwater runoff from other surfaces or by concentrated flue gases.

4.3 Bronze

Bronze is an alloy of 90% copper and 10% tin. Silver may be present in small quantities. Generally, its color is a salmon gold. However, this is seldom seen without the dark brown-red or green patina of the oxidized surface in corrosive urban or industrial atmospheres. Table 2 shows the effects of corrosive agents and the color of the patina they form on bronze components. Bronze has been used for casting sculptures, cannons, bells and other architectural elements such as doors since prehistoric times. Bronze reacts with alkalis such as ammonia and with various sulphurous compounds that combine with water to form sulphuric acid. Direct contact of copper with iron, steel, zinc, aluminium or galvanized steel may cause these metals to corrode.

In some situations the patina can be considered aesthetically valuable. Therefore, before any intervention measures are taken to remove the patina from the surface, the bronze object or structure should be carefully assessed.

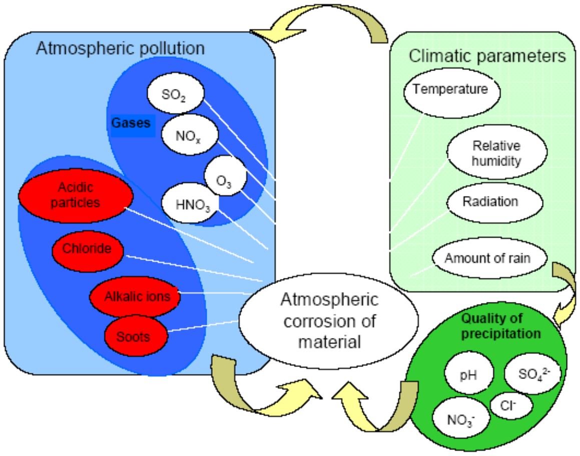


Figure 5 Environmental factors that affect metal corrosion [22]

5.0 BASIC CAUSES OF METAL CORROSION

Climatic parameters play a significant role in the corrosion of metals. Figure 5 shows that the temperature, humidity and rain have a significant influence on the condition of metals. When metals come in contact with gaseous pollutants and other reactive environmental agents, they chemically react to form different kinds of precipitates and slowly become corroded.

Sometimes allowances for corrosion are given in the design of a metallic object or structure by considering the possible duration of service life, the thickness of the material and other service conditions. Table 3 presents the influence of various conditions including humidity, temperature, rain, wind, impurities and metal wet times in different areas on corrosion rate [23]. Temperatures above 0^0C and relative humidity over 80% foster corrosion. Dissolved air impurities and adherent dust or dirt also facilitate atmospheric corrosion. The table below shows the uniform steel corrosion rate in different atmospheric conditions.

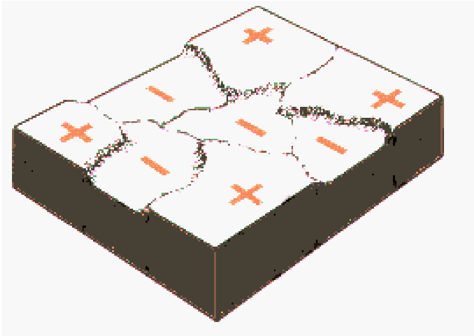
Table 3 Steel corrosion rates in various atmospheric conditions

Atmosphere	Corrosion rate (μm/year)
Rural	4-60
Urban	30-70
Industrial	40-160
Marine	60-170

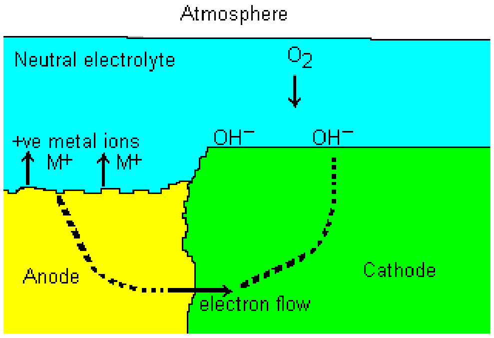
A layer of electrolyte on metal surfaces is one of the basic conditions for corrosion. Electrochemical reactions, anywhere from 5-150 μm, occur in this layer of electrolyte. If any amalgamation was done with two metals and if there is a fair difference between their positions in the electrochemical series, then corrosion will occur at the anode part [24].

Galvanic corrosion causes the oxidation of the anode metal and discharges electrons to the cathode metal, which remains undamaged (Figure 6) [25]. The following conditions must be present for the reaction to occur:

- A variance in electrochemical potential between two neighboring metals.
- The surface of the metal object should be covered in an electrolyte.
- An electrical track should be present to facilitate electron movement.



(a)



(b)

Figure 6 Schematic representation of galvanic influence on corrosion [10]

The water is disassociated into hydrogen ions and hydroxyl ions:

$$H_2O = H^+ + OH^- \quad (2)$$

Surface ionization takes place when a metal such as iron is posited in a liquid:

$$Fe = Fe^{++} + 2e^- \quad (3)$$

Ferrous ions moving away from the metal surface are further oxidized to ferric ions:

$$Fe^{++} = Fe^{+++} + e^- \quad (4)$$

These Fe^{+++} ions are attracted to the $(OH)^-$ ions and form the corrosion product $Fe(OH)_3$.

$$Fe^{+++} + 3(OH)^- = Fe(OH)_3 \quad (5)$$

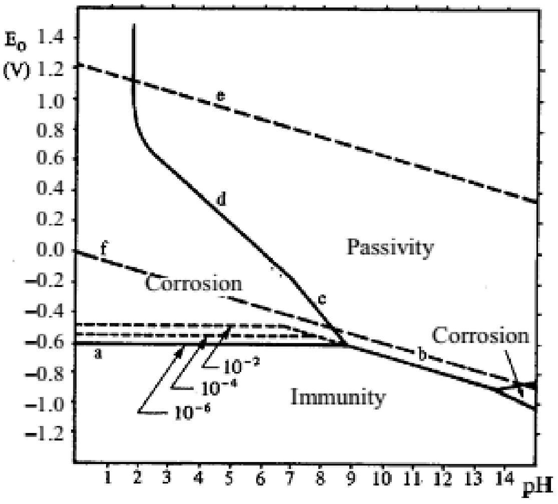


Figure 7 Pourbaix diagram for iron in water at 25⁰C [28]

5.1 Pourbaix Diagram

Marcel Pourbaix devised this diagram to represent the effect of pH on equilibrium potential. The diagram is generally used to illustrate corrosion possibilities [26-28]. The diagram in Figure 7 visualizes the states of iron when potential and pH are varied. When the potential is below the lines *a* and *b*, the metallic state is stable and the metal is immune to corrosion [29].

As can be seen from the diagram, the pH–potential plane is clearly divided into a corrosion region, a passivity region and an immunity region (Figure 7). There is also a small corrosion region at high pH, where the dissolved corrosion product is $HFeO_2^-$. The diagram can be used to determine the possible ranges of environmental pH and potential at which corrosion can be avoided.

5.2 Corrosion Under Oxygen Reduction

The presence of hydrogen and oxygen is essential for electrochemical reactions to take place [30]. Excessive amounts of H^+ ions in sufficient amounts for reactions to occur are only found in acidic environments [31]. Oxygen reduction is possible in neutral and alkaline mediums as electrochemical reactions are supported by the continuous dissociation of water.

$$4H_2O \rightarrow 4H^+ + 4OH^- \quad (6)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (7)$$

$$\text{Total reaction: } O_2 + 2\,H_2O + 4e^- \rightarrow 4OH^- \quad (8)$$

The oxygen reduction in acidic liquids is described by equation (7) and in neutral and alkaline solutions by equation (8). The reversible potential of the two reactions as a function of pH is represented by the same straight line in the Pourbaix diagram.

At a given pH value and 25°C the reversible potential is

$$E_0 = E^0_{0a} - \frac{0.059}{4} \log \frac{1}{p_{O_2} a^4_{H^+}} \quad (9)$$

$$= E^0_{0b} - \frac{0.059}{4} \log \frac{a^4_{OH^-}}{p_{O_2}} \quad (10)$$

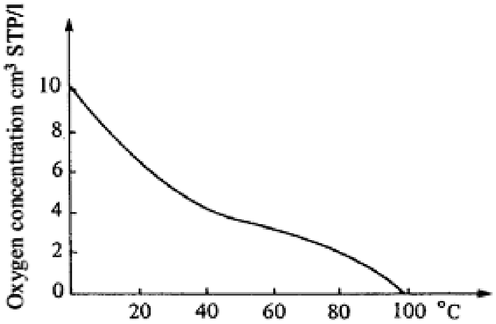


Figure 8 Concentration of oxygen in air-saturated water as a function of temperature [31]

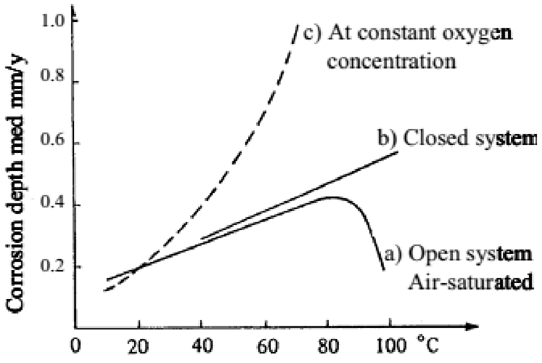


Figure 9 Corrosion of steel in water as a function of temperature [31]

5.3 Effect of Temperature

Temperature affects the exchange current density and the Tafel gradient. In natural environments, the most significant effect of temperature is often its effect on the diffusion-limiting current density *i*L [31, 32]. On surfaces without diffusion-limiting deposits, *i*L is expressed by:

$$i_L = D_{O_2 zF} \frac{c_B}{\delta} \quad (11)$$

The diffusion coefficient, D_{O_2}, depends strongly on the temperature:

$$D_{O_2} = Ae^{-Q/RT} \quad (12)$$

Where A and Q can be considered as constants in water, R the universal gas constant and T the temperature in K. The thickness δ of the diffusion boundary layer depends on different factors. For open systems where water is in equilibrium with the atmosphere, the oxygen concentration c_B is determined by the solubility, i.e. the saturation concentration, of air in the water. This concentration depends on the temperature, as shown in Figure 8. The effects of D and c_B together lead to the corrosion rate as a function of temperature as shown in Figure 9, curve a) for an open steel tank, with a marked maximum at about 80°C [31].

The thickness of the diffusion boundary layer depends on the flow velocity for a plane metal surface, which is shown in equations (10) and (12) [31]. The conventional Nernst's diffusion boundary layer (Figure 10) can be expressed by:

$$\delta = C\, f(L) Re^{-m} Sc^{-n} \propto V^{-m} \quad (13)$$

Where
Re is Reynolds' number = vL/Q,
Sc is Schmid's number = v/D,
v is the free flow velocity
L is a characteristic length and f(L) is a simple geometrical function

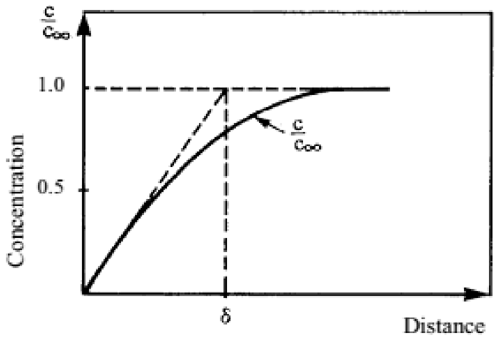


Figure 10 Nernst's diffusion boundary layer [33]

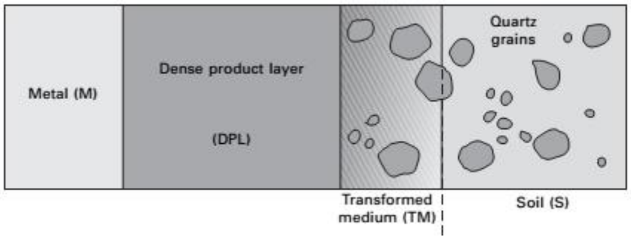


Figure 11 Corrosion pattern of archeological iron objects covered in earth [36]

5.4 Estimation of Average Corrosion Rate

The estimation of average corrosion rates (CR) is of great importance to predict the long-term corrosion of metals [16, 34-36]. Using this method an archeological iron artifact's corrosion can be calculated and its reliability can be verified by solubility calculation [37]. Figure 11 shows a diagrammatic representation of the corrosion pattern in buried archeological iron objects.

The corrosion rate can be obtained by dividing the iron equivalent thickness (t_{eq}) of the corrosion products by the age of the sample:

$$CR = \frac{t_{eq}}{age} \quad (14)$$

Iron equivalent thickness is calculated from the thickness of the corrosion products (dense product layer and transformed medium) corrected by the ratio of the density of the local medium and of iron as follows:

$$t_{eq\ Fe} = \int_0^{t_{soil}} mass\%\ Fe(t) \times \frac{\rho(t)}{\rho_{Fe}}\, dt \quad (15)$$

Where

t = distance from metal/corrosion products interface
dt = elemental variation of t
ρ(t) = density of medium (metal, corrosion products, soil) at t
ρ_{Fe}= density of iron (7.8 g·cm^{-3})
mass%Fe(t) = quantity of iron at *t* in mass%.

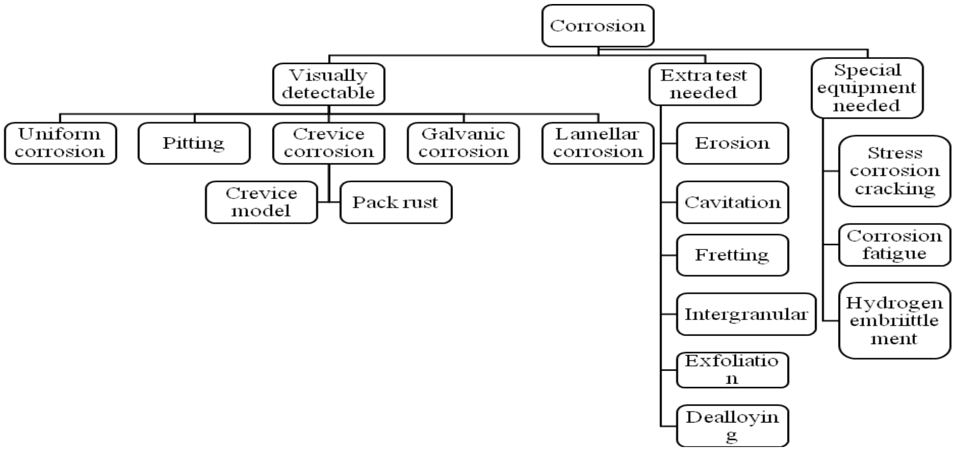


Figure 12 Various types of corrosion in different metals [31]

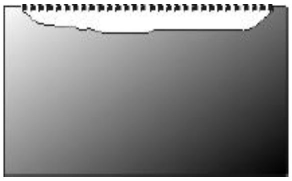
Another hypothesis, given by Vega E, Dillmann P, Berger P and Fluzin P [38], is that the transportation of oxygen in the water at the dense product layer pores is the limiting step in the corrosion mechanism. The corrosion rate can be evaluated using Faraday's law and taking into account the oxygen concentration gradient ΔC_{O_2} (mol/m^3), the thickness of the layer x_0 (m), the iron density μ_{Fe} (g/m^3), the molecular mass M (g/mol) and the apparent oxygen diffusion coefficient $D^*_{O_2}$ (m^2/s).

$$v_{corr} = \frac{D^*_{O_2} \Delta C_{O_2} M}{\mu_{Fe} x_0} \qquad (16)$$

6.0 CATEGORIES OF CORROSION IN HISTORICAL METAL

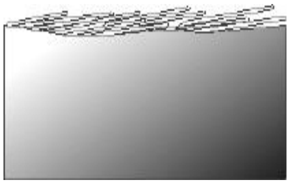
There are various types of corrosion in different metals (Figure 12). Corrosion may start with one type of corrosion, which can then lead to a series of worsening reactions where other types of corrosion attacks can become dominating factors [39]. The behavior and causes of corrosion can be found through careful investigation of the corroded sample while it is corroding, which may include microscopic examination of the surface of the metal object with the corrosion products intact and also after the corrosion products have been removed.

Figure 13 shows various types of corrosion that frequently occur on metals. These forms of corrosion are organized based on the simplicity of their detection. Some of these corrosions can be detected simply by visual inspection, such as uniform corrosion, whereas others need extra testing and special equipment, such as fatigue corrosion. Table 4 describes various categories of corrosion, their basic reasons of formation, significant attributes and possible remedial measures.

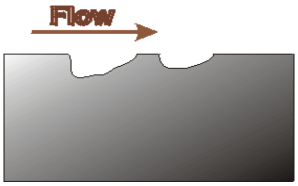


Uniform corrosion

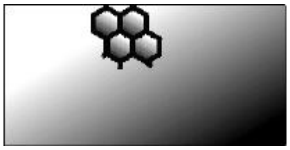
Pitting corrosion



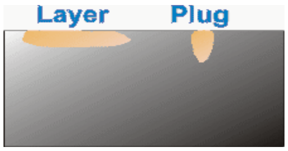
Lamellar corrosion



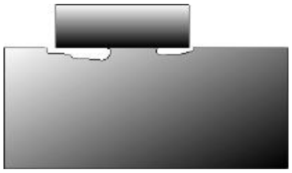
Erosion corrosion



Intergranular corrosion

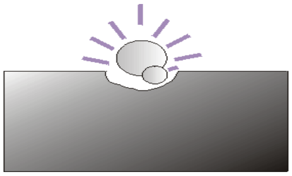


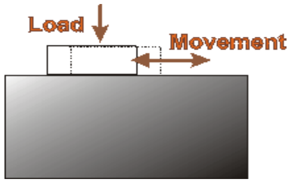
Dealloying corrosion

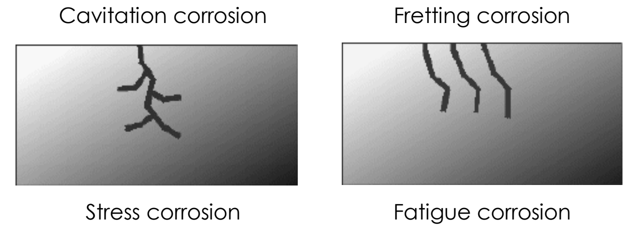


Crevice corrosion

Galvanic corrosion






Cavitation corrosion

Fretting corrosion

Stress corrosion

Fatigue corrosion

Figure 13 Major appearances of corrosions arranged by their ease of identification [31]

Table 4 Basic mechanism, characteristics and possible remedies of various corrosion types

Corrosion category	Causes	Important features	Remedy/comments
Uniform corrosion	Lack of substantial passivation tendency for homogeneous materials in actual environment [40].	The damage propagates quite evenly on the entire surface which causes a reduction in thickness.	Conventional protection methods such as coating, cathodic protection and environmental or material changes are possible remedial solutions.
Pitting	Occurs in passivated metals when electrode potential exceeds a critical value in an environment containing chloride, bromide and iodide ions [41, 42].	Narrow pits form with radiuses of the same order of magnitude. The pits may have different shapes but sharp boundaries. This is a serious condition as the pits may penetrate without clear warning and maximum pit depth increases with increasing surface area [41].	Appropriate materials that are sufficiently active against harsh environments provide the best protection. Cathodic protection also works.
Crevice corrosion	A localized mode of corrosion related to stagnant or even flowing liquid at the micro-environmental level that tends to occur in crevices. Most active in presence of chloride, though there is evidence of activity in other salt solutions.	Influenced by numerous factors such as metallurgy, environment, electrochemical, physical surface, geometrical nature and crevice gaps [42, 43].	Newer high-alloy steel with high M_o can be used instead of susceptible conventional metals (e.g. stainless steel). Crevices and possible deposition should be avoided (e.g. butt weld instead of overlap, straight-forward drainage paths). Cathodic protection is also possible.
Pack rust	A form of localized corrosion in crevices but develops in open atmospheric environments.	Rust packing appears between two steel plates, especially in steel bridges [44].	
Galvanic corrosion	Metallic contact between a more noble and less noble metal through an electrolyte causes corrosion to increase on the latter and decrease on the former [45].	Corrosion medium and temperature influence galvanic corrosion[46]. Aluminium and aluminium alloys are particularly prone to this type of corrosion [47].	The welded metal should be more noble than the base material. Blending of a large area of old material with a smaller area of new, more active material should be avoided. The two metals can also be insulated from each other or non–metallic distance pieces can be used. A metallic coating on one of the materials can also work.
Erosion corrosion	A relative motion between an eroding liquid and a submerged metallic object can cause the exposed material surface to mechanically wear away or erode [48].	Grooves or pits form according to the direction and condition of the flow. Usually occurs at comparatively high velocities between the material surface and the fluid [49].	Properly designing flow systems and other apparatus, filtering or precipitating solid particles, selecting suitable materials, applying corrosion-resistant coatings and using cathodic protection are possible preventive measures.
Cavitation	Similar to erosion corrosion but the appearance of the corrosion is different. It takes place when flow velocities are excessive and fluid dynamics cause large pressure variations [50].	Deep pits develop perpendicularly to the surface, often localized close to each other or grown together over smaller or larger areas, making a rough, spongy surface [51].	Possible remedies are using metals high in hardness and resistant to corrosion, increasing the fluid pressure to avoid gas bubbles, applying corrosion-resistant coatings, cathodic polarization and designing to avoid vibration.
Fretting corrosion	A minor repeated relative motion (slip) at the edge between two	May direct to more serious macroscopic motion between parts or initiate	Can be prevented by using lubricants (e.g. low-viscosity oil, molybdenum sulphide) or

	tightly fitted elements [52].	fatigue crack [53].	obstructing oxygen intrusion with gaskets or sealants.
Intergranular corrosion	Galvanic activity due to variances in impurity concentrations or alloying component materials.	Localized damage on or at grain borderlines with minor corrosion at other parts of the surface. Dangerous as the toughness of the substance is extremely reduced at a comparatively early phase, and a fracture can take place without notice [54, 55].	Intergranular corrosion occurs in stainless steels and alloys based on nickel, aluminium, magnesium, copper and cast zinc.
Stress Corrosion Cracking	Cracks form due to concurrent effects of static tensile stresses and corrosion [56]. The tensile stresses may originate from external loads or temperature changes, or they may be internal stresses induced by cold working or heat treatment [39, 57].	If cracks are not detected on time, they may cause fast unstable fracturing [16, 51]. Environmental, electrochemical and metallurgical factors as well as mechanical stress and strain are responsible for the mechanism and development.	Reducing the stress and stress intensity to below threshold values, making the environment less aggressive by removal of oxygen, distillation or ion exchange, using cathodic protection, supplying inhibitors and selecting the right materials are measures that can be taken to relieve this type of corrosion.
Corrosion fatigue	Cracks are stimulated by fatigue (variations in stresses) and are further accelerated by corrosion [58]. Varying tensile stresses causes this deterioration.	Fatigue fractures in non-corrosive environments exhibit large smooth crack surface areas where the cracks has grown by fatigue and an (often smaller) area with a rough and crystalline surface formed by fast fracturing when the maximum stress reached the ultimate strength [57, 59].	Measures to prevent this type of corrosion include reducing tensile stress levels as much as possible by stress annealing, applying reliable coatings on the highest fatigue areas, changing the environment by using inhibitors and de-aeration, selecting appropriate materials and proper designs, using moderate cathodic polarization and anodic protection.

7.0 CLASSIFICATION OF ENVIRONMENTS FOR CORROSION

Different environment have different levels of corrosiveness (Table 5) [60]. There are several standards that address the level and magnitude of corrosive environments [61, 62]. One of the defining standards for classification of corrosive environments is ISO 9223:1992, which classifies the corrosiveness of different atmospheres on various metals and alloys. Environments are organized based on three key factors: wet time, sulphur dioxide pollution and chloride content in air [63]. Guiding values for the corrosion rate of steel, zinc, copper and aluminium in the first three years are categorized in ISO 9224. Two other standards also categorize the corrosion of metals through the atmosphere and immersion. EN ISO 12944-2 classifies environments by their corrosive effects on steel structures protected by paints and varnishes. ISO 14713 discusses the protection of iron and steel structures against corrosion by using zinc and aluminum coatings.

Table 5 Corrosive effect of different environments on carbon steel and zinc

Corrosivity	Example environments	Carbon steel (μm/year)	Zinc (μm/year)
C1 (very low)	Indoor: Spaces with occasional condensation Outdoor: Inland rural	≤1.3	≤0.1
C2 (low)	Indoor: Dry spaces	1.3-25	0.1-0.7
C3 (medium)	Indoor: Spaces with high moisture content, few impurities Outdoor: inland urban, mildly saline	25-50	0.7-2
C4 (high)	Indoor: chemical industries, swimming pools, seaside docks Outdoor: very humid industrial plants, seaside urban areas	50-80	2-4
C5-I (very high)	Outdoor: very humid industrial atmospheres	80-200	4-8
C5-M (very high)	Outdoor: saline seaside atmospheres	80-200	4-8

8.0 COMMON TESTS FOR DIAGNOSIS

When any metallic artifacts are discovered, archeologists and scientists usually attempt to determine the main features and flaws of the heritage metal. This includes ascertaining the homogeneity of casting, critically thin areas, the structural continuity of joints indicating voids in the casting, previous repairs, and micro cracks. Various methods including non-destructive testing are employed to locate these aspects. Some of these methods are X-ray diffraction, ultrasonic testing, radiography thermo vision and acoustic emission. Chemical and electrochemical tests following different codes and standards are also used to determine the extent of corrosion and other mechanical and chemical properties of retrieved metallic artifacts.

(a) Bronze corrosion in sculpture (b) Cast iron corrosion in sculpture

(c) Lead corrosion in sculpture (d) Zinc corrosion in sculpture

Figure 14 Different forms of corrosion in historic artifacts [64]

9.0 CORROSION PROTECTION

Corrosion prevention usually involves the application of a coating. Cathodic protection using a zinc coating or galvanizing can also suppress corrosion. Widespread surface protection approaches are:

- Protective paint coating
- Electroplating
- Hot dip galvanizing
- Coil coating of sheet steel
- Rubberizing
- Spray galvanizing
- Chromium plating
- Aluminum spraying

An organic topcoat is sometimes applied to roofing or cladding products to enhance appearance and increase durability. The thickness of this coating may vary from 25-200µm. Paint is a barrier coating which generally provides enough corrosion protection for metals in many applications. However, paint containing red lead is toxic, thus, zinc phosphate paint is a better option. It is recommended that two coatings are applied. Examples of protective coatings that can be painted on are alkyd resin paints, chlorinated rubber and vinyl solvent paints, epoxy or polyurethane coatings. Zinc and aluminium coatings provide cathodic protection to iron.

Cast iron and wrought iron are of intrinsic value and it is thus preferable to repair as to renew objects and structures made from these materials [18]. Figure 14 shows different forms of corrosion on various historic artifacts. Repairing and preserving these historic metallic structures and artifacts is a better choice than removing them [13]. Historic fabrics and traditional materials and techniques should be maintained all through the consolidating process [64], which may include the use of additional materials or structures to reinforce, strengthen, prop, tie or support the existing object or structure.

Welding is not always possible for all metals. Excessive heat can cause recrystallization. It is inadmissible to weld large sections of cast iron on site. Wrought iron can be welded satisfactorily, and can be welded to steel and stainless steel. Cold repair methods include straps, threaded studs screwed into both sides of a fracture and dowels or plain pins. Seriously corroded, broken or missing castings may need to be recast. Gray cast iron should be replaced in the same material.

Where copper has been perforated, copper patches can be soft soldered over the hole. The patch should be large enough and correctly shaped to cover the area. The patch and holed sheet are seated together with continuous pressure applied to the patch during soldering. If the corrosion attack is in the early stages only the cause of the attack needs to be eradicated [65, 66].

Lead should never be repaired with solder as the different thermal expansion rates will cause the solder to break away. Lead in the edge zone tends to adopt a crystalline structure which does not accept welding. If deterioration is localized on the upper surface, the damaged section can be removed and replaced. Mastics or bituminous compounds cannot be used in repair because they obscure the source of the problem. The initial white patina of basic lead carbonate can be washed off. The formation of patina can be controlled by an application of patination oil.

Zinc sheet was once popular as roofing in France, Germany and Belgium. Zinc is less malleable than lead. Zinc roofing is initially bright, but with exposure to the atmosphere gradually develops a dark gray patina of zinc carbonate. The under surfaces can develop condensation corrosion. Zinc resists contact with other metals except copper and its alloys. It is prone to corrosion from sulphur products, acids and strong alkalis. The best way to clean zinc is with a brush and water. Zinc roofing is best left unpainted.

10.0 ANTICORROSION PAINTS

Before coating a metallic structure or object with protective paint, the surface to be painted must be perfectly clean. Surface preparation and cleanliness play a crucial role in the effectiveness of anticorrosion paints. There are several standards for the pretreatment before applying paints. The inspection procedure for steel surface cleanliness is discussed in ISO 8501-1 and ISO 8501-2. The standards for protective paint systems are stated in ISO 12944-1 to 8.

The preparation of a sound surface before applying protective paint involves the removal of old paint, rust, loose mill scale and soluble corrosion salts. The analysis of paint layers is part of the preparation program. Sound paint surfaces may simply be rubbed down. Small areas of paint can be removed with thixotropic paint strippers such as methylene chloride and their residues removed with white spirit. Flame cleaning and hot air blowers are also effective. Flame treatment is preferred in cleaning wrought iron as it removes only loose mill scale. In cleaning iron surfaces, the rust must be completely removed. Ferrous sulphate and chloride are water soluble, though not readily removed. The surface should be tested several times after each cleaning action.

11.0 CONCLUSIONS

Heritage structures and artifacts are a prime concern for peoples and nations around the world. The tangible and intangible elements of heritage are important as they are symbols of the history, culture, customs and glory of a nation. Cultural tourism is also now an established income generation source for any heritage enriched country. This has led to a pressing demand for the conservation and restoration of these historic forms and relics. In this paper an extensive survey of literature, including current studies, has been carried out. The main focus of this paper has been on the decay mechanisms and its remedial measures for historic metallic structures and objects.

Metals commonly used over the course of history have been studied for their manufacturing process, chemical composition, behavior and general usage. It was found that corrosion is the most common cause of decay in historic metallic structures and artifacts. The basic reasons for corrosion related problem and their guiding mechanisms were revealed in this study. Several guiding parameters which have great influence on the corrosion behavior of metallic structure were discussed. Among the most important factor influencing corrosion is the surrounding atmosphere. It plays a very important role in metal corrosion. Different atmospheric conditions cause the severity of the corrosion to vary. A classification of different atmospheres, their corrosiveness and their practical limits were presented in this study. Marine environments were found to be highly corrosive due to the presence of salt ions in the atmosphere. This paper also made a general classification of known corrosion problems, their impact and possible remedial measures. It was found that some types of corrosion (e.g. uniform, pitting, galvanic corrosion, etc.) are more common in heritage structures, whereas others appear rarely (e.g. cavitation, lamellar, intergranular corrosion, etc.). Conventional procedures such as coating and cathodic protection were found to be effective protection techniques. However, surface preparation and cleaning in accordance with standard guidelines are necessary before applying these techniques.

Some significant areas which need to be further explored in future studies are:

- More effective conservation techniques to protect metallic heritage structures located in marine environments need to be devised.
- Climatic changes threaten many cultural heritage structures around the world with accelerated decay. This issue needs to addressed globally and suitable measures need to be taken.
- The consequences of atmospheric pollution (SO_2, NO_x and other suspended particles) are ubiquitous. The levels of pollution need to be properly monitored and the effects on heritage structures and relics mitigated.
- Compatible, feasible and sustainable materials and intervention techniques which will maintain the historic fabric of heritage structures need to be investigated.
- The true scale of environmental impact on heritage structures within buildings, cities, sites, etc. needs to be assessed and controlled.
- A multidisciplinary knowledge based decision making system for the sustainable preservation of these heritage structures and artifacts needs to be established.

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