Study on the Influence of Galvanic Corrosion on Ship Structural Materials

Haifeng Zhang*
Jiangsu Maritime Institute, Nanjing 211170, China

*Corresponding author email: 496451713@qq.com

Abstract. In order to study the effects of galvanic corrosion on the structural materials of ships, the effects of metal corrosion and ballast tank coating failure on ships are discussed. The electrolytic treatment technology of ship ballast water is one of the mainstream technologies for ship ballast water treatment. The new corrosion system was carefully explored. The galvanic corrosion rate is related to the nature of the material itself, including the corrosion potential, corrosion current, and polarization properties of the metal before coupling. In addition, it is affected by factors such as the area ratio of the cathode and the anode, dissolved oxygen in the seawater environment, temperature, and flow rate. The results showed that the research on the galvanic corrosion behavior of typical structural materials of ships in the marine environment provided economic and effective protection measures for the protection of ship materials. Therefore, this method is of great theoretical and practical significance for the protection of metal structural materials in other industries.

Keywords: galvanic corrosion; ship structure; structural material.

1. Introduction
More and more electrolytic treatment technologies are finally approved and applied in real ships. Research on the effects of metal corrosion and ballast tank coating failures has become increasingly important and urgent [1]. The electrolytic treatment technology of ship ballast water has become one of the two mainstream technologies for ship ballast water treatment, and the other is based on processing technology. Due to the limited test period, some content is not perfect. The test should be further refined from the following aspects to obtain a more comprehensive coating corrosion protection mechanism [2]. The galvanic corrosion rate is related to the nature of the material itself (including the corrosion potential of the metal before coupling, corrosion current, polarization, etc.). In addition, it is also affected by factors such as the anode/anode area ratio, dissolved oxygen in the seawater environment, temperature, and flow rate. The cross-effect of these factors makes the galvanic corrosion problem extremely complicated [3]. New corrosion systems have been studied. The influence of different residual chlorine concentration solutions on metal corrosion and coating damage was explored. This has certain reference significance for anti-corrosion of ballast tanks.
2. State of the art
A variety of metal and alloy materials are used in marine and marine equipment structures. These metal and alloy materials are often present in the same structure or system in a combination (e.g., welded, bolted) [4]. Differences in potential will cause galvanic corrosion. Some metal components which have not obvious galvanic corrosion in atmospheric environment can undergo obvious galvanic corrosion in marine environment. In addition to accelerating the corrosion damage of the anode components, galvanic corrosion can also induce more dangerous corrosion damage in pitting, crevice corrosion, stress corrosion and other projects [5].

The theory of corrosion protection of existing ship ballast tanks is based on a metal seawater corrosion system. If the ship's ballast water is treated by electrolysis, the ballast tank may be in a new corrosion system for some time while the ballast water is being treated. It is unclear whether the corrosive medium will accelerate the failure of the ballast tank coating [6]. Therefore, this new corrosion system has been studied. This has important practical significance for the actual ship promotion of ballast water electrolysis treatment technology.

3. Methodology
Chemical corrosion refers to the damage caused by the direct purification of the metal surface and the non-electrolyte. The reaction characteristic is that the atom on the surface of the metal directly undergoes a redox reaction with the oxidant in the non-electrolyte to form a corrosion product. The transfer of electrons during the etching process is carried out directly between the metal and the oxidant. Therefore, no current is generated during the etching process. For example, the corrosion of high temperature steam on boilers is chemical corrosion.

\[
Fe + H_2O(g) \rightarrow FeO + H_2 \uparrow \\
2Fe + 3H_2O(g) \rightarrow Fe_2O_3 + 3H_2 \uparrow \\
3Fe + 4H_2O(g) \rightarrow Fe_3O_4 + 4H_2 \uparrow
\]

These reactions are all reversible reactions. At high temperatures, it is calculated from the thermodynamic data that the G value of the positive reaction is much smaller than zero, that is, the equilibrium reaction proceeds to the right.

The galvanic corrosion test is carried out according to GB/T15748-1995 "Test Method for Galvanic Corrosion of Marine Metal Materials". The three materials were combined into three pairs, 921A/B10, 921A/TA2, B10/TA2. The distance between the anode and the cathode in each pair was kept at 8 cm, and each group was tested with three parallel samples. The pair of samples and the saturated calomel electrode (SCE) constitute a three-electrode system. The corrosion current and the corrosion potential signal are collected by the DL-1 multi-channel galvanic corrosion tester, and the data is collected into a computer. The corrosion data is stored and recorded by the computer. Its working diagram is shown in Figure 1.

![Figure 1 Schematic diagram of galvanic corrosion](image-url)
According to the setting of the program, the data is collected every 60 minutes, and the test period is 10 days. Environmental parameters are measured periodically, including temperature, dissolved oxygen. During the test, the changes of the sample and the solution should be observed frequently and recorded.

4. Analysis and discussion of galvanic corrosion

4.1. Analysis of galvanic corrosion process

Electrochemical corrosion is the corrosion of a metal in an electrically conductive solution medium due to an electrochemical reaction. In the electrochemical reaction process, the generation of corrosion current is accompanied, and the electrochemical kinetics law is followed. Any corrosion reaction based on electrochemical mechanism includes at least one anodic reaction oxidation reaction that increases the valence of metallization and a cathodic reaction reduction reaction that decreases the valence of elements in a substance. Moreover, the ions flowing through the electrons and media inside the metal form a loop. The electrochemical corrosion of the metal is essentially the result of the short-circuit galvanic cell action, and the anodic reaction of this short-circuit cell destroys the metal material. However, since the metal itself has been short-circuited and cannot output electrical energy, the chemical energy of the redox reaction carried out in the corrosion system is completely lost in the form of heat energy. Such short-circuit primary batteries that cause destruction of metallic materials are collectively referred to as corrosion primary batteries. Electrochemical corrosion is the most common corrosion. The corrosion of metals in the atmosphere, sea water, soil and various electrolyte solutions is electrochemical corrosion.

The most fundamental cause of electrochemical corrosion of metals and composites in corrosive media is the presence of depolarizers in the corrosive media. Therefore, an unstable corrosive galvanic cell system is constructed. The cathodic reduction process of the depolarizer absorbs electrons generated by metal corrosion, which causes the metal to continuously suffer from corrosion. In the corrosion process of metals, there is always a cathode process in which the metal anode dissolves the enthalpy. Thus, the anodic corrosion process of the metal material is inevitably affected by the kinetics of the cathode process. Studying the various types of cathodic reactions that may occur in corrosive primary batteries in metal corrosion and their role in the corrosion process is necessary to understand the metal corrosion process. Electrochemical corrosion can be divided into hydrogen evolution corrosion and oxygen absorption corrosion from the mechanism.

Corrosion with hydrogen ion reduction as cathode process is called hydrogen depolarization corrosion or hydrogen evolution corrosion. If the potential of the metal is more negative than the equilibrium potential of the hydrogen electrode, there is a certain potential difference between the two electrodes. The metal and the hydrogen electrode constitute a corrosion original battery. The electrons emitted by the anode reaction are continuously sent from the anode to the cathode, causing corrosion of the metal. At the same time, hydrogen is continuously produced.

The anode reaction is:

$$2Fe \rightarrow 2Fe^{2+} + 4e^-$$  \hspace{1cm} (4)

The cathodic reaction is:

$$2H^+ + 2e^- \rightarrow H_2$$  \hspace{1cm} (5)

The necessary condition for the occurrence of hydrogen evolution corrosion is that the electrode potential of the metal must be lower than the reduction reaction potential of the hydrogen ion, that is, the hydrogen evolution potential $E_H$:

$$E_m < E_H$$  \hspace{1cm} (6)
Whether or not a metal will undergo hydrogen evolution corrosion in a given corrosive medium can be judged by the above calculation. Generally speaking, metals with lower potential, such as Fe and Zn, are in non-oxidizing acids without oxygen. Metals with very low potentials, such as Mg, undergo hydrogen evolution corrosion in neutral or alkaline solutions.

The results of the polarization curve test of metallic materials in natural seawater were obtained. After Cview fitting, the self-corrosion potential of 921A is stable at -718mV, and the self-corrosion potential of B10 is stable at -155mV. The self-corrosion potential difference between 921A and B10 is about 450mV. In theory, there is a large driving voltage between them. However, the actual driving voltage is the potential difference when the two metals are coupled to each other, and the driving voltage is also reduced after the coupling.

![Steady-state polarization curves of 921A and B10 in seawater](image)

**Figure. 2** Steady-state polarization curves of 921A and B10 in seawater

Figure 2 shows the polarization characteristics exhibited by 921A and B10 as a function of dissolved oxygen content in seawater. It can be seen that the 921A and B10 self-corrosion potentials have different degrees of positive shift depending on the increase of oxygen content. As the dissolved oxygen content in seawater increased from DO=0.2mg/L to DO=10.5mg/L, the corrosion potentials of 921A and B10 were shifted by 50mV and 120m, respectively.

**Table. 1** The fitting result of the polarization curve

| Dissolved oxygen content DO/mg/L | 921A          | B10          |      |
|-------------------------------|---------------|--------------|------|
|                               | Self-corrosion | Self-corrosion | Self-corrosion |
|                               | potential Esc/mV | current i/A•cm⁻² | potential Esc/mV | current i/A•cm⁻² |
| 0.2                           | -759          | 7.87E-6      | -291         | 1.31E-7       |
| 2                             | -751          | 4.57E-6      | -211         | 6.86E-7       |
| 4                             | -762          | 7.57E-6      | -201         | 1.82E-6       |
| 6                             | -726          | 2.06E-6      | -192         | 1.36E-6       |
| 7.5                           | -749          | 6.80E-6      | -199         | 3.17E-6       |
| 10.5                          | -705          | 2.07E-6      | -182         | 3.05E-6       |

4.2. Metal corrosion evaluation method

When the corrosion product satisfies the following conditions at the same time, it is suitable to adhere firmly to the sample and is almost insoluble in the solution. This is not contaminated by the external environment. At this time, the degree of corrosion damage can be measured by the weight gain method.
The weight gain method is suitable for assessing general and intergranular corrosion and is not suitable for other types of localized corrosion. One disadvantage of this approach is the indirect nature of the data. The data obtained includes the weight of the corrosion product and the amount of material. In addition, the composition of the corrosion product needs to be analyzed for conversion.

When corroded, the mass of the sample increases, and the corrosion product adheres completely to the surface of the sample. The weight gain method was adopted. Equation (7) is used to calculate the corrosion rate:

$$ V_{\text{increase}} = \frac{m_2 - m_0}{s t} $$

In the formula (7):
- $V_{\text{increase}}$: Corrosion rate (g/m$^2$h)
- $m_2$: Mass of sample with corrosion products (g)
- $s$: Surface area of the sample (m$^2$)
- $t$: Corrosion time (h)

This method is suitable for uniform corrosion. The corrosion product is completely detached or is easily removed from the surface of the sample. It is a simple and direct method. It does not require the corrosion products to adhere firmly to the surface of the material, nor does it take into account the solubility of the corrosion products. After the test, all corrosion products must be removed from the sample. The weight loss method directly indicates that the weight of the material lost due to corrosion does not need to be analyzed and converted by the chemical composition of the corrosion product. These advantages make it widely used.

4.3. Analysis of galvanic corrosion effects in ship structural materials

Currently, the two most important factors for coating failure are aging caused by exposure and metal corrosion under the coating. In addition, physical, chemical, and mechanical erosion are included. These advantages make it widely used. The aging of coatings is often characterized by loss of luster, discoloration, brittleness and cracking. The law of cracking and stress strain of the coating during the aging of the acrylic coating was investigated. The change in tension caused by day and night changes is the cause of cracking of the coating. Ultraviolet light plays a crucial role in accelerating the ageing of the coating. After exposure to ultraviolet light, some hydrophilic groups such as alkyl hydroperoxide, cyano group, etc. are formed, which accelerates the water absorption of the coating. Small molecules such as ketones, alcohols, acids, etc. are produced during photoaging. These small molecules are easily washed away, which renders the coating ineffective. Due to the constant loss of material composition, the coating shrinks and the thickness decreases, which leads to embrittlement and cracking. If the coating contains a pigment, the loss of the coating polymer will correspondingly increase the volume concentration of the pigment on the surface of the coating. As a result, the surface layer is relatively brittle, the inner layer is elastic, and the surface layer of the coating is powdered and deeply cracked.

The failure of coatings is not entirely due to the insufficient chemical stability of coatings, which leads to uniform depletion. Most of them are due to the penetration of the medium into the coating. The water absorption, bubbling, cracking and even shedding of the coating result in the loss of protective performance of the coating. Corrosive media can penetrate the interior of the coating, which is the effect of osmosis and stress. The results of the study indicate that the main cause of the coating failure is the slow penetration of the medium into the interior of the coating. The medium that penetrates the bonding surface of the coating and the metal substrate under the combined action of environmental stress will promote the micro-cracking to expand and even cause cracking. As the penetration of the medium progresses, the coating is often caused to bubble. There are currently two main types of data processing methods. One is to accurately analyze the measured data to obtain the parameters of each equivalent component. The other type is to evaluate the performance of the coating based on certain characteristic
values. For the first method, when fitting, the test data is regular and a suitable equivalent circuit is found.

5. Conclusion
The variation of coating capacitance obtained by equivalent circuit fitting indicates that residual chlorine has a greater influence on the diffusion rate of the second stage. When the concentration of residual chlorine is high, the diffusion rate of water and other active materials at the metal coating interface is fast, which greatly destroys the coating. This also indicates that residual chlorine accelerates the coating failure process. The metal protection effect of ballast tank will be better with the increase of coating thickness. However, too much coating thickness will prolong the painting time, and the consumption of paint will increase, which will cause unnecessary waste. Through testing, a suitable coating thickness was chosen for electrolysis of seawater. This can not only provide a better protection, but also save paint. It also has some reference significance for anti-corrosion of ballast tanks.

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