Simulation study on anti-corrosion performance of a ferroalloy flange

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Abstract. The corrosion problem of seawater pipeline is an important problem that ships need to face. Installing anticorrosive zinc block in seawater pipeline is a simple and practical anticorrosion means. In this paper, the anti-corrosion performance of a ferroalloy flange is simulated and analysed. The results show that, for the copper pipeline, both cathode current and anode current of the seawater pipeline using the copper - ferroalloy anticorrosive mode are significantly lower than those of the seawater pipeline using the copper - zinc alloy anticorrosive mode under the same external environment. This means that the anticorrosion performance of copper - ferroalloy model is obviously better than that of copper - zinc alloy model.

1. Introduction
Due to the perennial contact with sea water, the sea water pipeline of ships is faced with serious corrosion problem, which brings great safety hidden danger to the navigation of ships. In order to reduce the corrosion of pipelines, engineers have taken various measures. First, metal materials with stronger corrosion resistance are used as the materials for ship pipelines. For example, copper-nickel alloys with better corrosion resistance have been widely used in recent years to replace copper, brass and other materials as the materials for seawater pipelines[1-3]. The second is to take some anti-corrosion measures, such as the use of the cathodic protection of seawater pipeline. It is a cathodic protection law that sacrifices the anode to protect the pipeline from corrosion by corroding the anticorrosive zinc block. This method is simple to operate and widely used, but due to the rapid corrosion rate of zinc blocks, it is easy to cause the timely replacement, and the anti-corrosion effect is limited. This paper studies a kind of ferroalloy flange, which is used in the anticorrosion control of Marine sea water pipeline, and analyzes its anticorrosion performance through simulation analysis[4,5]. The Ferroalloy flange is shown in Figure 1.

Figure 1. Seawater piping with ferroalloy flange
2. Analysis of corrosion mechanism of seawater pipeline

The corrosion of metals in seawater is mainly electrochemical corrosion, which refers to the destruction caused by electrochemical reaction between metal surface and ionic conductive medium. In a reaction, a metal loses electrons and becomes an electron-deficient atom, known as a cation, and this readily oxidized metal electrode is called an anode. On the other hand, metal ions in solution are reduced or deposited as metal atoms on the surface of the electrode, called the cathode. A common metal protection measure is the cathodic protection law that sacrifices the anode. Sacrificial anode is corroded by replacing cathode with anode metal with high activation energy (low standard potential). Two different metals and electrolyte between the formation of a galvanic cell, cathode polarization. Taking the object of study in this paper as an example, due to the difference in corrosion potential between ferroalloy and copper, local corrosion at the contact point of the two in seawater was caused. The ferroalloy flange with low standard electrode potential is anode, and the copper with high standard potential is cathode. The activation energy of the anode is greater than that of the cathode, so it replaces the corrosion of the copper pipeline by seawater and achieves the effect of protecting the marine pipeline.

In the structure shown in Figure 1, the standard electrode potential of Fe and Cu is -0.44V and 0.337V respectively. So the ferroalloy as the anode of the galvanic cell, copper pipeline as the anode of the galvanic cell. In the sea water, the two constitute galvanic cells, the more active ferroalloy occurs redox reaction, the priority is to be corroded by sea water, so as to achieve the effect of protecting the copper pipe.

Among the objects studied in this paper, three electrochemical reactions occur on the boundary of copper: oxidation of copper, oxygen reduction and hydrogen evolution reaction of copper\[2,6]\:

\[
\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- ; \ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- ; 2\text{H}_2\text{O} + 2e^- \rightarrow 4\text{H}_2 + 4\text{OH}^- 
\]

In the electrochemical reaction process, Fe corresponds to Cu as the coupled anode, and the reaction occurs as follows:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- ; 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \uparrow ; \ \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \uparrow ; \ \text{Cu} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2 \uparrow 
\]

As shown in the above formula, the reaction of the cathode produces hydrogen gas. And, as seawater is amphoteric, it can be separated as an acid or base by the following reaction:

\[
\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- 
\]

Hydrogen evolution is more frequent because seawater itself produces hydrogen ions. At the same time, Fe and Cu also lose more electrons, leading to the current increase and continuous corrosion of materials.

3. The simulation analysis

The structure of Cu-ferroalloy as shown in Figure 1 was simulated and analyzed by using COMSOL multiphysics simulation software to analyze its corrosion resistance, and the corrosion resistance of the structure was compared with that of Cu-Zn alloy\[7,8]\.

3.1 Model assumes

The model in Figure 1 is simplified as follows:

(1) The electrochemical field is a steady state field. It is assumed that all activation energy losses during charge transfer are zero. There's no change in potential at any point.

(2) Obey Ohm's law

This is, \( q = -\delta \nabla \phi \).

(3) The electrolyte satisfies the principle of neutrality. That is, the net charge anywhere in the electrolyte is zero.

(4) Corrosion is only related to the conductivity and oxygen content of seawater, and other factors are not considered, and they are considered to be only related to the location, that is, for a certain location, the seawater conductivity and dissolved oxygen content in the pipeline are fixed values.
(5) Only electrochemical corrosion is considered, and the influence of sea water flow on corrosion is not considered.

(6) Since the corrosion of the sea pipeline is mainly seawater corrosion in the pipeline and occurs on the inner surface, the scope of study is narrowed down to the inner surface of the pipeline.

(7) Ignore changes in pipe thickness due to corrosion, i.e. pipe diameter is fixed.

(8) According to the symmetric boundary, the object of study is simplified into two solid cylinders with different materials and different lengths but closely connected. The longer one represents the copper pipe, the shorter one represents the simplified ferroalloy flange, and the solid part of the cylinder represents seawater. As shown in Figure 2.

![Figure 2. Simplified simulation model](image)

### 3.2 Build a model

Physical quantities required for modeling as following:

1. the exchange current density $i_0$: For the same electrode, when the electrode reaction is in equilibrium, the reaction speed of anode and cathode is equal, and the absolute value of the current density generated is called the exchange current density. The exchange current density is an intrinsic property of the electrode and is only related to it. It is often used to indicate the ability of an electrode to gain or lose electrons, or how easy it is for the electrode to react.

2. equilibrium potential: When the oxidation rate is equal to the reduction rate, that is, the charge exchange rate is equal to the material migration rate, the whole reaction system forms a thermodynamic equilibrium state. The electrode potential at this point is called equilibrium potential. It can directly reflect the equilibrium state of the electrode.

   It can be seen from the above reaction, hydrogen is released from the metal surface with the occurrence of corrosion. Therefore, Tafel formula can be used to calculate the current density. According to the distribution of current density, the corrosion of the pipeline can be obtained. Tafel formula is as follows:

   $$\eta = a + b \log i$$

   Among them, $\eta$ is overpotential.

   $a$ is the overpotential when the current density is equal to $1\text{A/cm}^2$.

   $b$ is the slope of Tafel.

   $i$ is corrosion current density.

   $a$ and $b$ are related to electrode material surface state, temperature and electrolyte concentration.

   After referring to the corresponding parameters, the above formula can be simplified in combination with the research object

   $$i_x = -\frac{C_{x}}{C_{x, ref}}i_{0, x} \times 10^{A_x \eta_x}$$

   Among them, $C_x$ is the concentration of x.

   $A_x$ is the Tafel slope.

   $\eta_x$ represents overpotential.

3. Sea water oxygen saturation: The conductivity of seawater at different locations is related to the diffusion coefficient of oxygen. As shown in Table 1.
Table 1. Relationships among the oxygen saturation of sea water, conductivity and oxygen diffusion coefficient

| Sea water oxygen saturation | Sea water conductivity (S/m) | Oxygen diffusion coefficient |
|-----------------------------|-----------------------------|------------------------------|
| 0.2                         | 0.000175                    | 152e-10                      |
| 0.3                         | 0.000815                    | 115e-10                      |
| 0.4                         | 0.002                       | 83e-10                       |
| 0.5                         | 0.004878                    | 49e-10                       |
| 0.55                        | 0.005882                    | 39e-10                       |
| 0.6                         | 0.007042                    | 28e-10                       |
| 0.65                        | 0.008                       | 20e-10                       |
| 0.7                         | 0.009804                    | 15e-10                       |
| 0.75                        | 0.0125                      | 10e-10                       |
| 0.8                         | 0.015625                    | 8.5e-10                      |

3.3 The boundary conditions

Choose the potential of the iron anode as the ground. The polarization generated by the Fe anode is ignored and the electrolyte potential is obtained:

\[ \Phi_1, \text{Fe} = -E_{eq}, \text{Fe} + \Phi_s, \text{Fe} = -E_{eq}, \text{Fe} \]

\[ E_{eq}, \text{Fe} \] is the empirical measurement of equilibrium potential of ferroalloy electrodes in the pipeline. The value is -0.76V.

The oxygen concentration in the pipe is assumed to be constant. The general concentration of seawater oxygen can be used as the rated value of oxygen concentration, which is taken as 5.2g/mol.

The three electrochemical reactions occurring on the cuprous boundary were modeled by the electrode surface nodes in the secondary current distribution interface. Border on this, with no applied voltage, so think of white brass electric \( \Phi_{\text{Cu}, \text{Cu}} \) is 0 v.

Tafel formula can be used to express the reaction equation of copper pipeline as follows:

\[ \eta_{\text{Cu}} = i_{\text{0Cu}} \times 10^{A_{\text{Cu}} \eta_{\text{Cu}}} \]

\[ i_{\text{O2}} = - \frac{C_{\text{O2}}}{C_{\text{O2, ref}}} i_{\text{0O2}} \times 10^{A_{\text{O2}} \eta_{\text{O2}}} \]

\[ i_{\text{H2}} = - i_{\text{0H2}} \times 10^{A_{\text{H2}} \eta_{\text{H2}}} \]

According to Table 2, the over-potential of the corresponding electrochemical reaction is calculated by the following formula:

\[ \eta = \Phi_{\text{s, Cu}} - \Phi_1 - E_{eq} \]

Table 2. Electrochemical reaction parameters

| parameter               | unit   | Cu    | O2    | H2   |
|-------------------------|--------|-------|-------|------|
| equilibrium potential, \( E_{eq} \) | V      | 0.337 | 0.189 | -1.03 |
| Exchange current density, \( i_0 \)   | A/m²   | 2×10⁻⁷ | 7.7×10⁻⁷ | 1.1×10⁻² |
| Tafel slope, \( A \)                      | V/decade | 0.41  | -0.18 | -0.15 |
3.4 Model parameters
COMSOL multi-physical field simulation software was applied to select the secondary current distribution model, and its modeling parameters were shown in Table 3.

| Name      | Expression | Value   | Description                      |
|-----------|------------|---------|----------------------------------|
| A_Cu      | 0.41[V]    | 0.41V   | Tafel slope iron oxidation       |
| A_H2      | -0.15[V]   | -0.15V  | Tafel slope hydrogen evolution   |
| A_O2      | -0.18[V]   | -0.18V  | Tafel slope oxygen reduction     |
| C_O2_ref  | 8.6[mol/m³] | 8.6mol/m³ | Oxygen reference concentration |
| Eeq_Cu    | -0.76[V]   | -0.76V  | Iron oxidation equilibrium potential |
| Eeq_H2    | -1.03[V]   | -1.03V  | Hydrogen evolution equilibrium potential |
| Eeq_O2    | 0.189[V]   | 0.189V  | Oxygen reduction equilibrium potential |
| i0_Cu     | 7.1e-5[A/m²] | 7.1E-5A/m² | Iron oxidation exchange current density |
| i0_H2     | 1.1e-2[A/m²] | 0.011A/m² | Hydrogen evolution current density |
| i0_O2     | 7.7e-7[A/m²] | 7.7E-7A/m² | Oxygen reduction exchange current density |
| Eeq_Fe    | -0.68[V]   | -0.68V  | Fe equilibrium potential        |
| PS        | 0.6        | 0.6     | Pore saturation                  |
| E_app     | 0[V]       | 0V      | Applied cell potential          |

3.5 Analysis of simulation results
The current densities of anode and cathode of Cu-Fe and Cu-Zn alloy pipelines are obtained through the above modeling.

(1) Cu-Fe alloy
(a) Local current density of copper
(b) Local current density of Ferroalloy
Figure 3. Copper - ferroalloy current density

(2) Cu-Zn alloy
(a) Local current density of copper
(b) Local current density of Zinc alloy
Figure 4. Copper - Zinc alloy current density
By comparing the cathode local current density of Figure 3 (a) and Figure 4 (a), it is found that the cathode current of the combination of Cu-Zn alloy is about 4 ~ 7 times that of Cu-Fe alloy. According to Faraday's Law: for a single electrolytic cell, in the electrolytic process, the amount of oxide precipitates on the cathode is directly proportional to the current intensity and conduction time. The formula is as follows

\[ M = KQ = KIt \]

Where, \( K \) stands for the proportionality constant, \( Q \) for the amount of electric quantity passed, \( I \) for the current, and \( t \) for the time.

It can be seen from the above formula that the greater the cathodic corrosion current is, the faster the cathode material is consumed. Conversely, the lower the corrosion current, the slower the cathode material consumption. Therefore, the cathodic anticorrosion effect of Cu-Fe alloy pipeline is far better than that of Cu-Zn alloy combination.

By comparing the anode local current density in Figure 3 (b) and Figure 4 (b), it is found that the anode current of the Cu-Zn alloy combination is about 3 ~ 4 times that of the Cu-Fe alloy anode current. Similarly, according to Faraday's law, when the ferroalloy of Cu-Fe alloy pipeline is sacrificed as an anode, the consumption per unit time is far less than the anodic zinc alloy of Cu-Zn alloy.

4. Conclusion
The anti-corrosion performance of a ferroalloy flange is studied in this paper, and the conclusion is that the given ferroalloy flange is superior to the anti-corrosion zinc block in both the anti-corrosion of the cathode and the durability of the anode.

References
[1] Kear G, Barker B D, Stokes K. Electrochemical corrosion behavior of 90-10 Cu-Ni alloy in chloride based electrolytes[J]. Journal of Applied Electrochemistry, 2004(34): 659-669.
[2] Sun Baoku. Galvanic corrosion and electric insulation between different materials of seawater pipelines[D]. Ocean University of China, 2009.
[3] Li Shikai. Study on corrosion resistance of new Cu-Ni-Al alloy in artificial seawater[D]. Henan University of Science and Technology, 2017.
[4] Shen Hong, Gao Feng, Zhang Guangen. Material selection and anti-corrosion measures of seawater piping in warship[J]. Ship Engineering, 2002(4): 43-47.
[5] Xin Shibao. Review in corrosion and protection methods of seawater pipeline of marine ships[J]. Equipment Environmental Engineering, 2018,15(11): 98-101.
[6] Xia Lanyan, Huang Guiqiao, Zhang Sanping. Marine corrosion and protection of metal materials[M]. Beijing, Metallurgical Industry Press, 2003.
[7] William B J Z. Modeling and analysis of multiphysical field by finite element method[M]. Beijing, China Communications Press, 2015.
[8] Wang Lei, Dong Lina. Simulation analysis of stray current corrosion based on COMSOL multiphysics[J]. New Technology & New Process, 2014(1): 22-24.