

Short Communication

Investigation of Q235 low-carbon steel corrosion under simulated ballast water tank conditions

Hao Sun, Junxia Li and Ning Chen*

Energy and Power School, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu, China

*E-mail: ecsi_chen@163.com

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To study the corrosive effect of an inert flue gas deoxygenation treatment of ship ballast water on ballast tanks, a total immersion corrosion test was employed. Under the simulated corrosive environment of the ship ballast tank, different corrosive media with a dissolved oxygen (DO) degree of 0.5 mg/L, a pH value of 6, a DO concentration of 0.5 mg/L and a pH value of 6 were used to simulate seawater. After the marine low-carbon steel Q235 was immersed in different media for 792 h, the corrosion law of the low-carbon steel Q235 was explored for ships with the most suitable conditions for inactivating microorganisms by inert flue gas deoxygenation. Specifically, the dissolved oxygen content of ballast water was 0.5 mg/L and the pH value was 6. The results show that in the ballast water treated with inert flue gas N₂ and CO₂ with a DO concentration of 0.5 mg/L and a pH value of 6, the corrosion rate of the sample was reduced by 69.02% compared to that of the sample in the simulated seawater. There were fewer corrosion products and little black pitting, of which the open circuit potential was relatively positive, and the resistance to corrosion was better. The polarization curve shifted to the right, and the tendency of corrosion was significantly reduced. Under the optimal process conditions for the inert flue gas treatment of microbes in ballast water, that is, a DO concentration of 0.5 mg/L and a pH value of 6, the ballast water after the inert flue gas treatment reduced corrosion in the ballast tank.

Keywords: inert flue gas deoxidation method; ship ballast tank; sea water; corrosion

1. INTRODUCTION

The process of unloading ballast water during ocean voyages is biologically invasive and causes serious damage to the ecological environments of various countries[1-7]. The current technical methods for ballast water treatment include mechanical, physical and chemical methods[8-14]; however, the existing technology for treating single ship ballast water cannot meet the IMO standards, is not practical, effective, or economical and does not consider matters of safety or environmental protection. The method of treating ballast water by inert flue gas deoxygenation[15-18], which desulfurizes and denitrates the flue gas discharged by ships during navigation, generates inert flue gas with a lower

oxygen content (including N₂, CO₂, and a small amount of O₂ and other gases). Then, the inert flue gas is applied to the ballast water of a ship, and this addition can reduce the DO concentration and pH value of the ballast water and destroy the microorganisms in the ballast water[19-21]. The method improves the energy utilization rate, is environmentally friendly and saves energy. However, the decrease in the dissolved oxygen and the pH value of the ballast water changes the corrosion system of the ballast tank. There are few studies on the treatment of ballast water with inert flue gas deoxygenation and the effect on the metal corrosion of ship ballast tanks. A total immersion corrosion test, which occurred in a simulated ship ballast tank corrosion environment, was performed in this paper, and the conditions that were most suitable for destroying microorganisms with inert flue gas were examined. Furthermore, the corrosion mass loss method, morphology observation method, and electrochemical measurement technology were utilized to analyse the corrosion law of marine low carbon steel Q235 after it was immersed in different corrosive media with a DO concentration of 0.5 mg/L, a pH value of 6, simulated seawater, a DO concentration of 0.5 mg/L and a pH value of 6 for 792 h.

2. EXPERIMENT

2.1 Experimental materials

2.1.1 Simulated seawater

The simulated seawater in this experiment was configured according to the Mocledon artificial seawater formula. The temperature ranged from 18 °C to 25 °C, and the salinity ranged from 25.5 to 35.5. The contents of each component are shown in Table 1.

Table 1. Artificial seawater formula

Molecular Formula	Content (g/L)
NaCl	26.726
MgCl ₂ 6H ₂ O	2.260
MgSO ₄ 7H ₂ O	3.248
CaCl ₂	1.153
NaHCO ₃	0.198
KCl	0.721
NaBr	0.058
H ₃ BO ₃	0.058
Na ₂ SiO ₃	0.0024
Na ₂ Si ₄ O ₉	0.0015
H ₃ PO ₄	0.002
Al ₂ Cl ₆	0.013
NH ₃	0.002
LiNO ₃	0.0013

2.1.2 Corrosion test specimen

The corrosion test specimen was marine low-carbon steel Q235. The specimen size was divided into the following types: 10 mm×10 mm×3 mm and 50×25 mm×3 mm. The former was used to analyse morphology and perform electrochemical research, and the latter was used for mass loss analysis. Table 2 illustrates the chemical composition of the specimens.

Table 2. Chemical composition of specimens

Chemical composition	C	Si	Mn	S	P
	≤0.22	0.12-0.30	0.03-0.65	≤0.045	≤0.045

2.2 Experimental system

The experimental system for treating ballast water by the inert flue gas deoxygenation method is shown in Figure 1. The test device includes a flue gas simulation system, a filtration system, a gas–liquid mixing system, and a simulated ballast tank system. The flue gas is simulated by pure CO₂ and N₂, and the gas flow is adjusted by the Qixing mass flow controller. During the test, the simulated seawater volume was 100 L, and the simulated delivery pump used a centrifugal pump with a rated flow of 1.5 m³/h. The simulated flue gas and simulated ballast water are mixed through the venturi tube to form a high-pressure water flow[22-23]. The inert flue gas forms a cavity in the water flow, and then the cavity absorbs dissolved oxygen in the ballast water. Next, the cavity rises and its buoyancy causes the water surface to overflow, so the dissolved oxygen in the ballast water is changed. The function of the simulated ballast tank breathing valve is to maintain a slight positive pressure in the ballast tank. According to the law of partial pressure and the law of total pressure, since the partial pressure of N₂ and CO₂ in the simulated flue gas is greater than the pressure of the dissolved oxygen in the simulated ballast water, the dissolved oxygen in the simulated ballast water overflows.

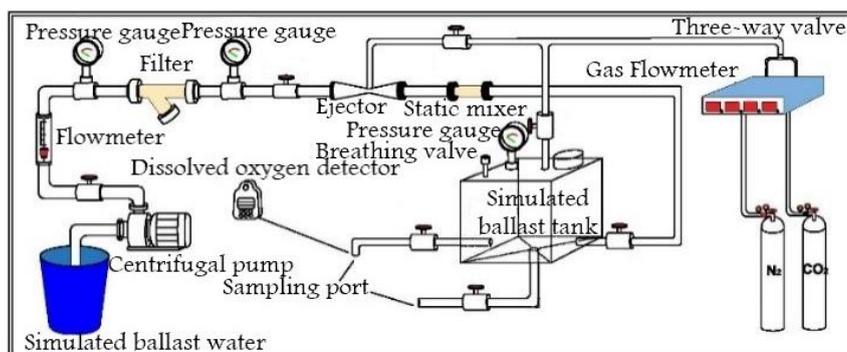


Figure 1. Schematic diagram of the experimental system

2.3 Experimental device

2.3.1 Flue gas simulation device

In the experiment, the parameters of each gas in the simulated flue gas were as follows: high purity nitrogen, $N_2 \geq 99.999\%$; filling pressure, 12.5 ± 0.5 MPa (20°C); carbon dioxide, $CO_2 \geq 99.9\%$; and filling pressure, 12.5 ± 0.5 MPa (20°C). In the experiment, to better simulate the properties of inert flue gas, in the mixture of nitrogen and carbon dioxide, the volume flow ratio of nitrogen and carbon dioxide was set to 7:1.

2.3.2 Filter system

In this experiment, the Y-type filter was used to remove impurities contained in the working fluid.

2.3.3 Mixing gas-liquid device

Mixing gas-liquid device consists of an ejector and a static mixer.

2.4 Experimental method

The test adopts the full immersion corrosion test by referring to the mechanical standard JBT7901-2001 "Metal Material Laboratory Uniform Corrosion Test Method".

The corrosion test was carried out under the most favourable conditions for inactivating microorganisms in inert flue gas (a DO concentration of 0.5 mg/L and a pH value of 6). The volume flow ratio of nitrogen and carbon dioxide was adjusted through a gas flow metre, which can change the corrosive medium of the ballast tank. Thus, the ballast tank environment contained corrosive media at a DO concentration of 0.5 mg/L with a pH value of 6 and a DO concentration of 0.5 mg/L with a pH value of 6. The corrosion data of low-carbon steel Q235 for ships after immersion in four different corrosive media with a DO concentration of 0.5 mg/L, a pH value of 6, a DO concentration of 0.5 mg/L and a pH value of 6 and simulated seawater for 792 h were collected.

Each group of experiments used 3 parallel test pieces that were suspended in a simulated ballast tank and immersed, and the experiment was carried out at room temperature.

2.5 Sample analysis method

The mass loss experiment was performed as follows: before the test, the wet samples were ground with sandpaper, washed with deionized water, degreased with acetone, and dried in air. After drying, the mass of the sample was accurately measured. After the sample was removed from the corrosive medium, the loose corrosion products were immediately washed away with water, wiped dry, wiped with anhydrous alcohol, air dried and weighed.

The morphological observation method was performed as follows: the macro-topography was imaged with a digital camera, and the micro-topography was observed with a scanning electron microscope.

The electrochemical test was performed as follows: the electrochemical test used a conventional three-electrode system for the tests, including the open circuit potential test and polarization curve test. The sample corroded by different corrosive media was the working electrode, the auxiliary electrode was the electrode-high-purity platinum sheet, and the reference electrode was the saturated calomel electrode (SCE).

3. RESULTS AND DISCUSSION

3.1 Corrosion factor

After the inert flue gas treatment, the changes in corrosion factors in different corrosive media were obtained and are shown in Table 3.

From the test results in Table 3, it can be seen that the temperature, salinity, and conductivity of the seawater did not change significantly after the inert flue gas treatment, and the changed factors were only the treatment factors. According to the literature[24-25], the environmental factors that affect the corrosion of metals in seawater are mainly the salt content, conductivity, dissolved substances, pH value, temperature, flow rate and waves, and organisms in the seawater. During the test, the flow rate and waves were not simulated because the movement of simulating seawater does not add microorganisms. Therefore, it can be inferred that after the inert flue gas treatment, in different corrosive media, the corrosion of ballast tank materials is only related to the treatment factor, that is, the corrosion change of the ballast tank material in the corrosive medium with a DO concentration of 0.5 mg/L after inert flue gas treatment is only related to the change in dissolved oxygen; the corrosion change of the ballast tank material in the corrosive medium with a pH value of 6 after inert flue gas treatment is only related to the pH value; and the corrosion change of the ballast tank material in the corrosive medium with a DO concentration of 0.5 mg/L and a pH value of 6 after inert flue gas treatment is only related to the change in the DO concentration and the pH value.

Table 3. Changes in some corrosion factors in seawater after the inert flue gas treatment

Corrosion factor	Simulated seawater	DO concentration=0.5 mg/L	pH= 6	DO concentration=0.5 mg/L & pH=6
	Test group	Treatment group	Treatment group	Treatment group
Temperature/°C	18.1~23.2	19.5~23.7	19.8~24.2	18.5~24.5
Salinity/PSU	31.2~37.6	31.4~38.3	31.3~37.9	31.5~38.1
pH	8.13	8.12	6.04	6.02
Conductivity /ms·cm ⁻¹	44.12	44.19	44.21	44.23
DO concentration/mg·L ⁻¹	7.25	0.5	7.19	0.52

3.2 Mass loss experiment

The results of the corrosion mass loss test with different corrosive media are shown in Table 4. Among them, v_1 , v_2 , and v_3 are the corrosion rates of three parallel specimens in each group of tests, and v_a is the average corrosion rate of the specimens. It can be seen that in the corrosive medium with a DO concentration of 0.5 mg/L, the average corrosion rate of the sample is the lowest; in a corrosive medium and in a corrosive medium with a pH value of 6, the average corrosion rate of the sample is the highest. Compared with the samples in simulated seawater, the average corrosion rate of the sample is reduced by 69.02% in the corrosive medium with a DO concentration of 0.5 mg/L and pH of 6.

Table 4. Results for the corrosion mass loss of samples in different corrosive media

Corrosive medium	$v_1/$ (mm/a)	$v_2/$ (mm/a)	$v_3/$ (mm/a)	$v_a/$ (mm/a)
Simulated seawater	0.121	0.075	0.142	0.113
pH=6	0.018	0.014	0.015	0.016
DO concentration=0.5 mg/L	0.259	0.115	0.113	0.163
DO concentration=0.5 mg/L & pH=6	0.036	0.034	0.035	0.035

Based on the above analysis, the corrosion of metals in seawater is mainly controlled by oxygen depolarization. If the oxygen in the seawater is completely removed, the metal will not corrode[26-27]. Therefore, the average corrosion rate of the sample in the corrosive medium with a DO concentration of 0.5 mg/L is the lowest among the rates. The pH value of seawater also affects corrosion, and it mainly affects the deposition of calcium scale on the surface of metal, which has a relatively high resistance and hinders the diffusion of oxygen to the cathode surface, thereby inhibiting metal corrosion. Furthermore, the decrease in pH value will increase the H⁺ concentration, which will accelerate hydrogen depolarization corrosion, so the average corrosion rate of the sample is the highest in a corrosive medium with a pH value of 6. In the corrosive medium with a DO concentration of 0.5 mg/L and a pH value of 6, the decrease in pH value affects the deposition of calcium scale on the surface of the metal and accelerates corrosion by hydrogen depolarization. In addition, seawater deoxygenation greatly reduces corrosion by oxygen depolarization, so the overall average corrosion rate is reduced compared with the average corrosion rate of the sample in the simulated seawater.

3.3 Morphology observation method

3.3.1 Macro morphology

The macro-morphology of the sample after corrosion in different corrosive media was imaged by a digital camera and is shown in Figure 2.

Figure 2 shows that in the corrosive medium with a DO concentration of 0.5 mg/L, the surface of the sample is covered with a slightly lighter yellowish brown colour. According to the literature[28], the sample was in the initial stage of corrosion, mainly because the decrease in the DO concentration can greatly reduce metal corrosion. In contrast, obvious yellowish-brown spots appeared on the surface of the sample in a corrosive medium with a DO concentration of 0.5 mg/L and a pH value of 6, and the number of covered yellowish-brown corrosion products increased. This phenomenon is caused by the increase in acidity of the corrosive medium, which increases corrosion by hydrogen depolarization.

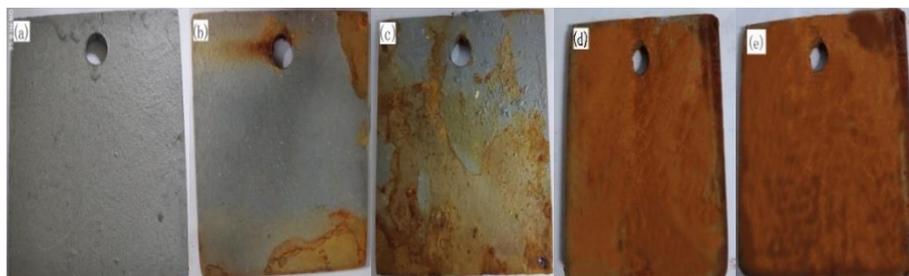


Figure 2. Macroscopic morphology of the sample after corrosion in different corrosive media (a. non-corroded sample, b. DO concentration=0.5 mg/L; c. DO concentration=0.5 mg/L & pH=6 d. simulated seawater, e. pH=6)

In the simulated seawater, the corrosion products on the surface of the sample contain a multilayer structure. The overall red, brown, and black colours of the corrosion products are mixed with each other. The structure is loose and easily falls off. In contrast, the thickness of the corrosion product from the sample in the corrosive medium with a pH value of 6 increases, and the corrosion is more severe. This may be because the pH value of the corrosive medium is reduced, which intensifies the cathodic corrosion by hydrogen depolarization. It can be seen from the sample macro-morphology results that the corrosion results are consistent with the results calculated by the mass loss experiment.

3.3.2 Microscopic morphology

After removing the corrosion products from the sample, a scanning electron microscope (SEM) was used to observe the microscopic morphologies of the sample after corrosion in different corrosive media. The results are shown in Figure 3.

Figure 3 (b) shows that in the corrosive medium with a DO concentration of 0.5 mg/L, black pitting appears on the surface of the sample. According to research results in the literature[29-30], the corrosion of the specimen is in its infancy. Figure 3 (c) shows that in the corrosive medium with a DO concentration of 0.5 mg/L and a pH value of 6, the black pitting corrosion on the sample surface increases compared to that of the sample in the corrosive medium with a DO concentration of 0.5 mg/L. The pitting corrosion pits are gradually connected. The reason for this phenomenon may be that the increase in H^+ aggravates the cathodic corrosion of steel by hydrogen depolarization, resulting in more pitting

corrosion, and the corrosion range is enlarged. As seen in the simulated seawater in Figure 3 (d), there are fewer pitting corrosion pits, and irregular grooves appear on the surface of the sample. In Figure 3 (e), it can be seen that in the corrosive medium with a pH value of 6, more and more irregularities appear on the surface of the sample. Compared with the sample in the simulated seawater, the groove is deeper; this is mainly because in the corrosive medium with a pH value of 6, the sample undergoes not only oxygen absorption corrosion but also hydrogen evolution corrosion, which intensifies the corrosion of the metal. Based on the corrosion micromorphology, it can be seen that the results are consistent with the results calculated by the mass loss experiment and macro-morphology.

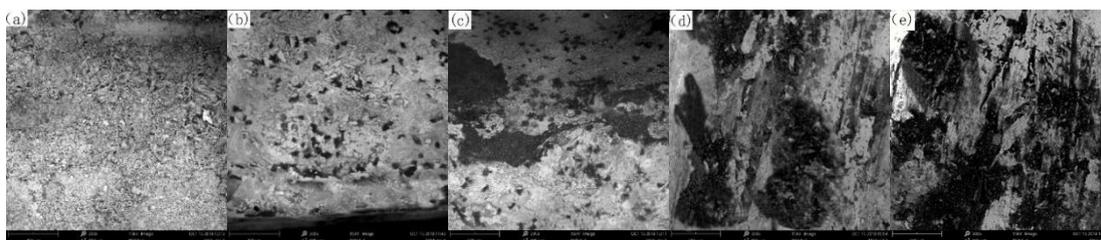


Figure 3. Macroscopic morphology of the sample after corrosion in different corrosive media (a. non-corroded sample; b. DO concentration=0.5 mg/L; c. DO concentration=0.5 mg/L & pH=6 d. simulated seawater; e. pH=6)

3.4 Electrochemical test

3.4.1 Open circuit potential

In different corrosive media, the curve of the corrosion potential of carbon steel with time was determined and is shown in Figure 4.

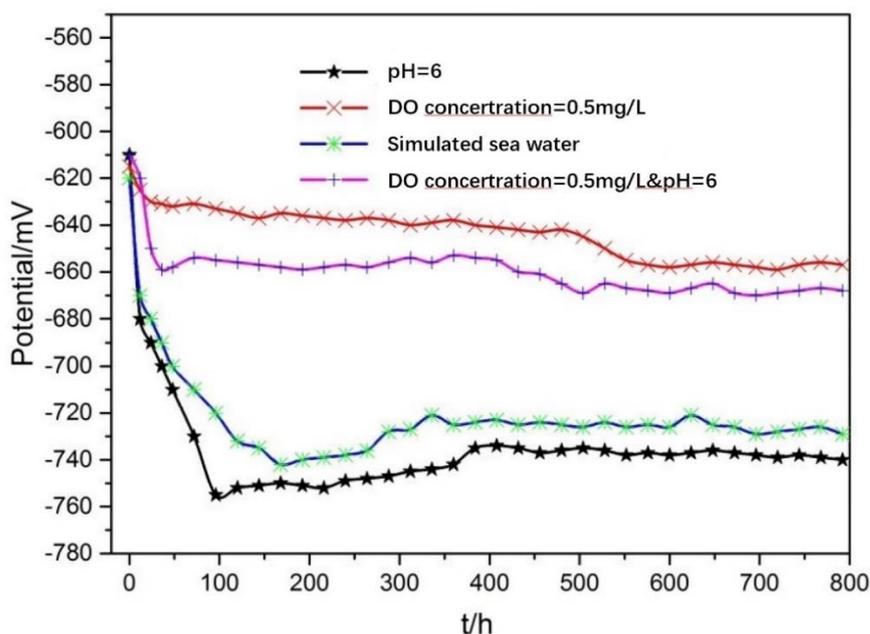


Figure 4. Open circuit potential-time curve of samples in different corrosive media

The experimental results show that the potential of the samples in different corrosive media has an initial negative shift; with increasing test time, the potential has a positive shift and finally reaches a stable potential. Compared with the potential in other corrosive media, the sample has the most negative potential in the corrosive medium with a pH value of 6, which is -755 mV. In a corrosive medium with a DO concentration of 0.5 mg/L, the potential is more positive than the most negative potential in the other corrosive medium, which is -651 mV.

In summary, due to the corrosiveness of the corrosive medium, the oxide film on the surface of the carbon steel is destroyed, and the effective corrosion area increases, so the anodic reaction transitions from weak to strong, and the potential incurs a negative shift. In the corrosive medium at a pH value of 6, the potential reaches the highest negative value, and the potential is positive in the corrosive medium with a DO concentration of 0.5 mg/L, a DO concentration of 0.5 mg/L and a pH value of 6. As the immersion time continues, the rust layer formed by the oxidation of the metal material adheres to the surface of the material so that the anode reaction is blocked, and the potential incurs a positive shift. Then, when a stable rust layer and electric double layer has formed on the metal surface, the potential begins to stabilize.

According to the research results of the literature[31-33], for steel materials, the more positive the corrosion potential in seawater corrosive media is, the better the corrosion resistance may be. Compared with the test results in this paper, the sample in the corrosive medium with a DO concentration of 0.5 mg/L has the best resistance to corrosion. Therefore, when protecting metal materials in ballast water, removing dissolved oxygen in seawater can be considered.

3.4.2 Polarization curve

The polarization curves of the samples in different corrosive media are shown in Figure 5.

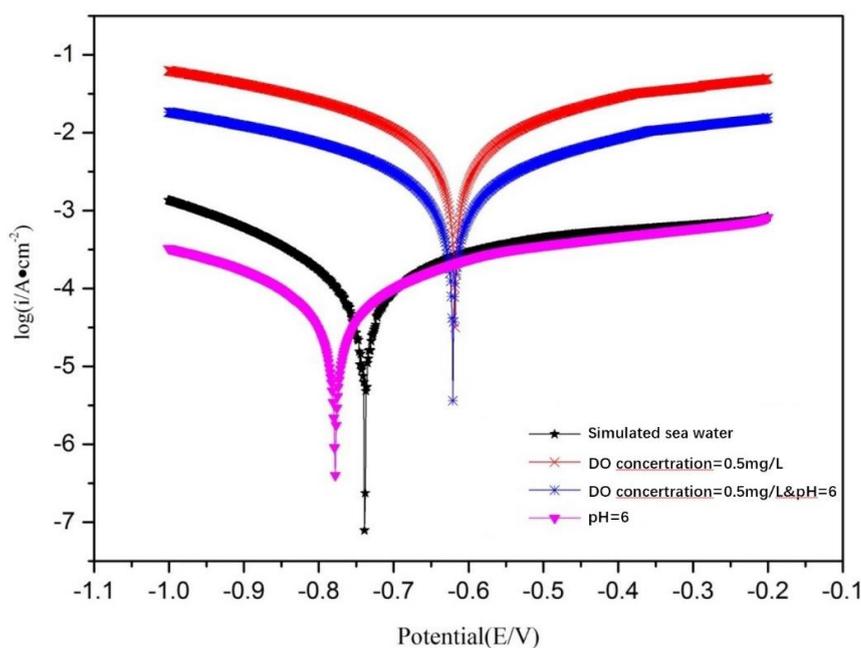


Figure 5. Polarization curve of the sample in different corrosive media

Compared with the sample in simulated seawater, the polarization curve of the sample in the corrosion medium with a DO concentration of 0.5 mg/L obviously shifts to the upper right, and the self-corrosion potential has a positive shift. In addition, the anodic polarization curve shifts significantly downwards and its slope decreases, indicating that the anode has an obvious polarization phenomenon; the metal dissolution reaction is hindered, the corrosion reaction rate drops rapidly, which is consistent with the results of the open circuit potential test, and the tendency for corrosion is reduced[34].

Compared with the polarization curve for the sample in the simulated seawater, the polarization curve of the sample in the corrosive medium with a pH value of 6 is slightly shifted to the left, the sample tends to be more severely corroded, and the corrosion rate rises slightly. Compared to the sample in the simulated seawater, the polarization curve of the sample in a corrosive medium with a DO concentration of 0.5 mg/L and a pH value of 6 obviously shifts to the upper right, and the self-corrosion potential has a positive shift.

Parameters including the corrosion potential E_{corr} and corrosion current I_{corr} after polarization curve fitting are shown in Table 5. From Table 5, it can be concluded that the cathode Tafel slope (B_c) and anode Tafel slope (B_a) of the sample electrode in a corrosion medium with a DO concentration of 0.5 mg/L are higher than the cathode Tafel slope (B_c) and anode Tafel slope (B_a) of the sample electrode in simulated seawater, indicating that both the cathodic reduction reaction and the anode dissolution reaction on the surface of the sample electrode in a corrosive medium with a DO concentration of 0.5 mg/L have an inhibitory effect.

Table 5. Electrochemical parameters of the corrosion of samples in different corrosive media

Corrosive media	E_{corr}/V	$I_{corr}/\mu A$	B_a/mV	B_c/mV
Simulated seawater	-0.745	10.654	87	148
pH=6	-0.792	11.572	84	124
DO concentration=0.5 mg/L	-0.541	5.467	95	151
DO concentration=0.5 mg/L & pH=6	-0.546	6.234	93	145

According to the above analysis, in ballast water with a DO concentration of 0.5 mg/L that was treated with inert flue gas N_2 and ballast water with a DO concentration of 0.5 mg/L and a pH value of 6 after that was treated with inert flue gas N_2 and CO_2 , the corrosion tendency of the carrier water was reduced compared with that of the simulated seawater samples. Therefore, under the optimal conditions for the inert flue gas treatment of microbes in ballast water, the treatment reduced the corrosion in the ballast tank.

4. CONCLUSION

1) The inert flue gas deoxygenation method was used to treat ship ballast water, and the temperature, salinity, and conductivity of the seawater medium before and after treatment were not

changed significantly, and the change factor was the only treatment factor. It is inferred that the change in corrosion of the metal materials in the ballast tank is related to the decrease in DO concentration and the increase in pH value in the treated seawater.

2) In ballast water with a DO concentration of 0.5 mg/L that was treated with inert flue gas N₂, the corrosion rate of the sample was the lowest, the sample surface had fewer corrosion products, and a small amount of black pitting appeared. In addition, the open circuit potential was the most positive, and the corrosion resistance was the best. The polarization curve shifted to the right, and the tendency of corrosion was significantly reduced because the deoxygenation of seawater greatly reduces corrosion via oxygen depolarization. Therefore, when protecting metal materials against corrosion in seawater, the removal of dissolved oxygen in seawater can be considered.

3) In the ballast water with a pH value of 6 that was treated with inert flue gas CO₂, the corrosion rate of the sample was the highest, the corrosion products on the surface of the sample increased, the corrosion was severe, the open circuit potential was the most negative, the polarization curve shifted to the left, and the corrosion tendency significantly increased. This may be because the pH value of the corrosive medium was reduced, which intensifies the corrosion via cathodic hydrogen depolarization.

4) In the ballast water treated with inert flue gas N₂ and CO₂ with a DO concentration of 0.5 mg/L and a pH value of 6, the corrosion rate of the sample was reduced by 69.02% compared to that of the sample in the simulated seawater. There were fewer corrosion products and little black pitting, the open circuit potential was relatively positive, the corrosion resistance was better; the polarization curve shifted to the right, and the corrosion tendency was significantly reduced. Therefore, under the optimal process conditions for the inert flue gas treatment of ballast water with microorganisms, that is, a DO concentration of 0.5 mg/L and a pH value of 6, the ballast water after the inert flue gas treatment reduced corrosion in the ballast tank.

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