

Investigation of Corrosion Behavior of Q235 Steel in Simulated Industrial Wastewater

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Different from the corrosion in the natural seawater, there are many factors influencing the metal corrosion of facilities along the sea entrance. Due to the large amount of anions in industrial wastewater, its discharge has a great influence on the corrosion of port facilities. In this paper, open-circuit potential (E_{ocp}), AC impedance spectroscopy and potentiodynamic polarization curves were used to characterize the corrosion behavior of Q235 steel influenced by three kinds of anions. The concentrations of the anions were set as $[Cl^-]$ 20000mg/L, $[HCO_3^-]$ 200mg/L and $[SO_4^{2-}]$ 3000mg/L, with reference to the maximum value of the industrial wastewater discharged from Yantai sea area. The result showed that at the given concentration, the corrosion of Q235 steel was inhibited in the Cl^- solution, whereas in the HCO_3^- solution and SO_4^{2-} solution, the corrosion was inhibited at first and then promoted later in the experiment.

Keywords: Carbon steel; Industrial wastewater; Corrosion resistance; Seawater environment

1. INTRODUCTION

Material corrosion exists in various environments, and one of the common reason is due to the influence of sodium chloride, the representative salt and other anions in seawater. Due to the defects of impurities in metal materials, the passivation film on the metal surface will be destroyed in case of some active anions (Cl^- , HCO_3^- , SO_4^{2-} , etc.) in the medium adsorbed on the metal surface, thus corrosion occurs. Nowadays, with the strategic development transferred from land to ocean and the increasing exploitation of marine resources, coastal ports are under rapid development. Metal corrosion and failure will inevitably occur due to long-term exposure to severe marine environments[1-4].

The industrial wastewater discharged from industrial production process contains various anions, leading to the damage of the structure and properties of materials, and even huge potential safety hazards

and property losses. A lot of research have been done on the corrosion mechanism of marine engineering materials. Chen[5] studied the dissolution kinetics of Fe in acidic chlorides by potentiodynamic polarization curves, and it showed that at constant pH, the increase of chloride concentration would accelerate the dissolution rate of metal. Allam[6] reported that with the increase of metal thickness, the permeation film of chloride ions became thinner, which reduced the corrosion rate of materials. Wu[7] proposed that the corrosion rate of Q235 steel increased with the increase of CO_3^{2-} content in the solution, but decreased when the corrosion rate exceeded its maximum. Liu[8] analyzed the polarization curves and found that the corrosion rate of Q235 steel was accelerated with the increase of SO_4^{2-} content in soil. However, most of the work were focused on the influence of single anion on the material corrosion.

In this work, considering the corrosion characteristics of steel facilities under the condition of industrial wastewater discharge and simulating the type and concentration of anions contained in industrial wastewater, the effect of anions on the corrosion behavior of Q235 steel were analyzed by electrochemical means. The purpose of this work is to enrich the corrosion mechanism, provide theoretical basis for strengthening the management and construction of port facilities and to realize the optimal allocation of resources.

2. EXPERIMENTAL SECTION

2.1 Material

The main chemical compositions of Q235 steel in the experiment is listed in Table 1. The samples were processed into a $10 \times 10 \times 2$ mm sheet. The copper wire was connected with the sample by solder and sealed in a cylindrical cavity filled with epoxy resin, leaving an exposure surface of 1cm^2 as a working electrode. Before the experiment, the surface of the sample was polished with 240 to 1200# sandpapers, then rinsed with distilled water and degreased with acetone. The samples were placed in a deoxygenation chamber and tested after UV disinfection for 30 minutes.

Table 1. Chemical compositions of Q235 steel

Element	C	Mn	Si	P	S	Fe
Content(wt%)	≤ 0.16	$\leq 0.53\%$	≤ 0.30	≤ 0.04	≤ 0.055	bal

2.2 Electrochemical measurements

The natural seawater used in this work was taken from Yantai sea area. The concentrations of the anions added were set as $[\text{Cl}^-]$ 20000mg/L, $[\text{HCO}_3^-]$ 200mg/L and $[\text{SO}_4^{2-}]$ 3000mg/L, with reference to the maximum value of the industrial wastewater discharged from Yantai sea area.

The electrochemical workstation(PARSTAT2273, USA) was used for electrochemical analysis. The Q235 steel was used as working electrode, a platinum-niobium wire with a diameter of 4 mm used

as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. After stabilization of the system, the open circuit potential was measured. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 10^{-2} - 10^5 Hz and the amplitude of the sinusoidal voltage signal was 10 mV. The electrochemical polarization curve was tested and scanned after immersion for 192h. The scanning rate was 0.33 mV/s, and the scanning range was ± 350 mV relative to the open-circuit potential. The data were analyzed and processed by ZSimpWin, C-View and Origin software.

3. RESULTS AND DISCUSSION

3.1 OCP measurement

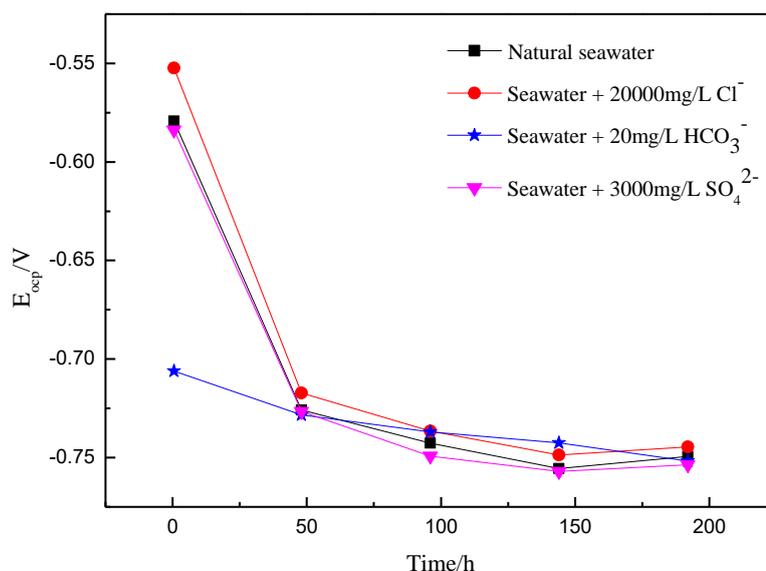


Figure 1. The change of E_{ocp} of Q235 steel in different solutions over time

Fig.1 shows the change of E_{ocp} of Q235 steel in different solutions over time. It can be seen that the potential values of Q235 steel were close to each other in the natural seawater system and the other two system with Cl^- and SO_4^{2-} addition, and the trend was almost the same. There was a significantly negative shift in E_{ocp} in 48 hours, and then it remained stable in the later stages. In the system with HCO_3^- addition, the initial E_{ocp} was more negative for the change of pH value and it gradually shifted negatively in 192h, indicating that the corrosion was aggravated[9-11]. Generally, the oxygen absorption corrosion of Q235 steel occurred within 48h in all systems. With the consumption of dissolved oxygen, the potential tended to be stable within 48h to 192h with a slightly negative shift, and finally stabilized at about -0.75V.

3.2 EIS measurement

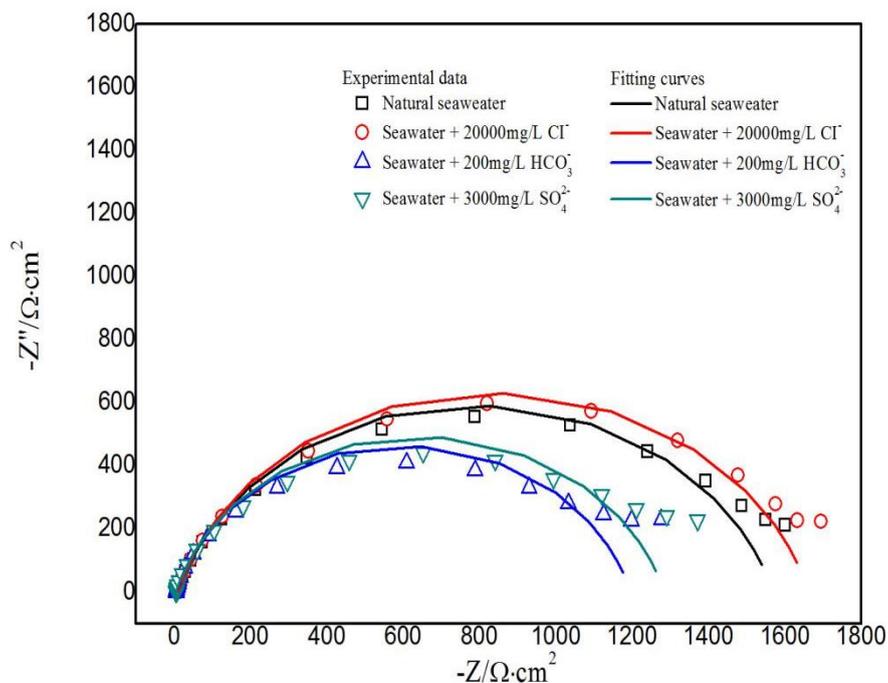
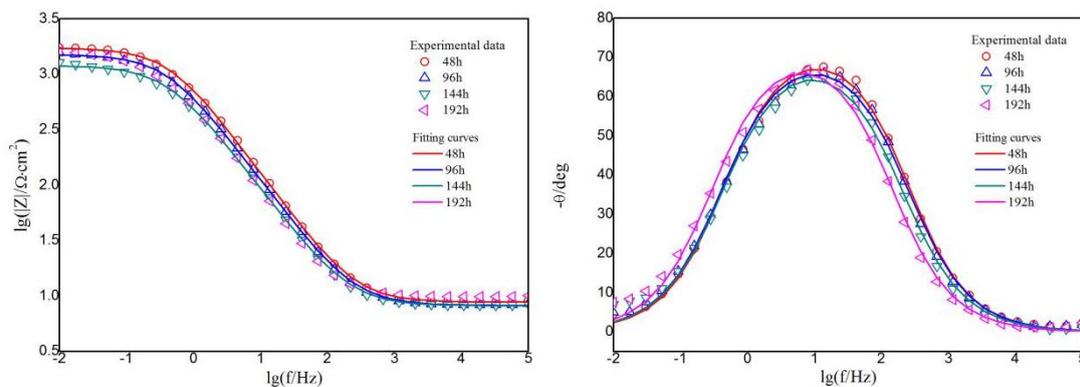


Figure 2. Nyquist diagram of Q235 steel immersed in four different systems for 192h

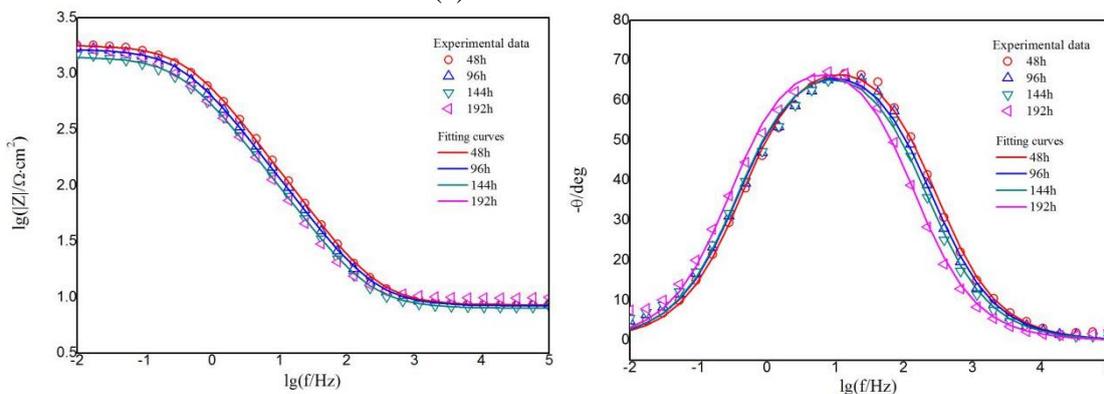
Fig.2 shows the Nyquist diagram of Q235 steel immersed in different solutions for 192 hours. It is seen from the Fig.2 that all the diagrams presented semicircular arcs, indicating that Q235 steel had capacitive characteristics in four systems[12]. The capacitance arcs were irregular due to the "dispersion effect" caused by the film inhomogeneity on the electrode surface.

By comparison of the four systems, the radius of capacitive arc in the system with Cl⁻ addition was the largest, revealing the steel had the largest resistance and the smallest corrosion tendency in the system. However, the radius of HCO₃⁻ solution system and SO₄²⁻ solution system were smaller, which indicated that the resistance of Q235 steel decreased and the corrosion rate were faster than that in the natural seawater system. It was reported[13-15] that when Q235 steel was immersed in seawater system, oxide layer would generally develop on the surface and prevent from further corrosion. However, the addition of HCO₃⁻ and SO₄²⁻ would lead to the change of pH value and destroy the oxide layer thus accelerate corrosion. The reduction reaction of HCO₃⁻ played an important role in the cathode process, and this process was controlled by activation.

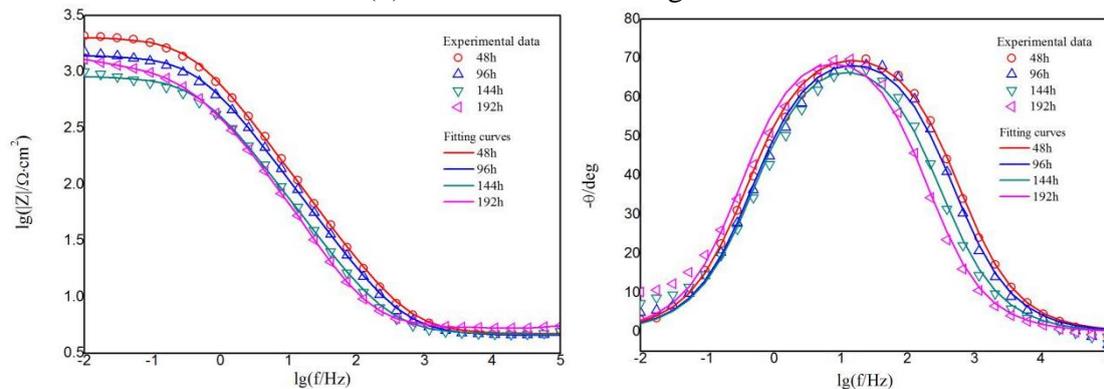
With the increase of corrosion, the corrosion products on the electrode surface increased, the thickness of oxide layer decreased, the contact area of metal and exterior increased, and the corrosion sensitivity increased. While in the system of seawater with Cl⁻ addition, the concentration of Cl⁻ was high and the capacitive characteristics was obvious, which could delay or prevent the penetration of Cl⁻ into the metal, increase the corrosion resistance and decrease the corrosion tendency[16].



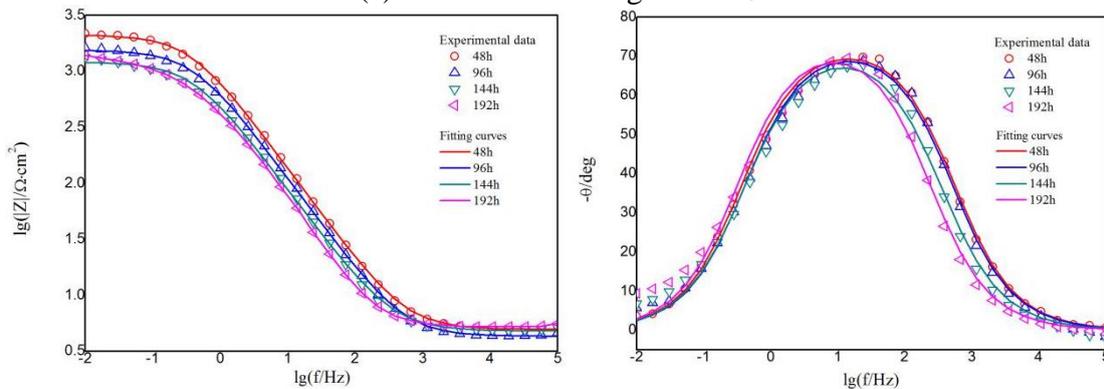
(a) Natural seawater



(b) Seawater + 20000mg/L Cl⁻



(c) Seawater + 200mg/L HCO₃⁻



(d) Seawater + 3000mg/L SO₄²⁻

Figure 3. Bode diagrams of Q235 steel immersed in four different solutions

Fig.3 shows the bode diagram of Q235 steel immersed in four different solution systems for different time (48h-192h). There was only one time constant in all four systems, and the peaks were at lower frequency. In addition, during the whole experiment, the impedance modulus of Q235 steel changed slightly. As the impedance modulus was generally proportional to the corrosion resistance of metals, it showed that the corrosion of Q235 steel tended to be stable with the consumption of dissolved oxygen.

ZSimpWin software was used to fit the EIS diagram with the corresponding equivalent circuits, as shown in Fig.4. R_s represents electrolyte resistance, Q_{dl} represents the double layer capacitance, n represents the capacitance coefficient and R_{ct} represents the charge transfer resistance[17]. The results of fitting parameters are shown in Table 2.

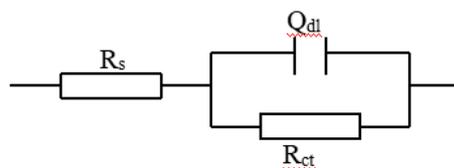


Figure 4. The equivalent circuit models used to fit the EIS experimental data for Q235 steel immersed in four different solutions

Table 2. Parameter fitting values of each element in the equivalent circuit in Fig.4

Medium	t (h)	R_s ($\Omega \cdot \text{cm}^2$)	$Q_{dl} \times 10^{-4}$ ($\Omega^{-1} \cdot \text{cm}^{-2}$)	n	R_{ct} ($\Omega \cdot \text{cm}^2$)
Natural seawater	48	8.79	2.48	0.83	1720
	96	8.19	3.04	0.82	1510
	144	8.13	3.74	0.81	1199
	192	9.74	3.77	0.83	1560
Seawater + 20000mg/L Cl^-	48	8.55	2.44	0.82	1793
	96	8.39	2.97	0.82	1657
	144	8.00	3.55	0.81	1417
	192	9.78	3.64	0.83	1654
Seawater + 200mg/L HCO_3^-	48	4.71	2.34	0.83	2039
	96	4.56	2.90	0.83	1403
	144	4.65	4.28	0.82	910.3
	192	5.29	4.72	0.84	1189
Seawater + 3000mg/L SO_4^{2-}	48	4.95	2.35	0.83	2120
	96	4.29	2.92	0.83	1556
	144	4.80	3.80	0.82	1220
	192	5.29	4.72	0.84	1189

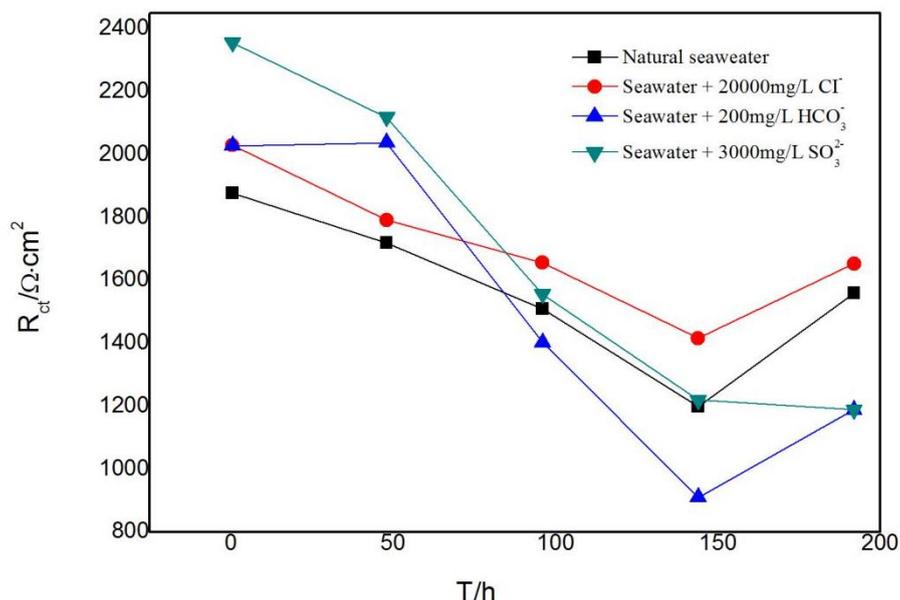


Figure 5. Comparison of the R_{ct} values between seawater and different Systems

By comparing the R_{ct} in four systems as shown in Fig.5, the values at the same time were close and the trend was almost the same. There was a continuous decrease within 0-144 h, indicating that the steel was in the state of accelerated corrosion. However, within 144-192 h, an increase of R_{ct} indicated that the corrosion reaction was inhibited by the consumption of dissolved oxygen, and an inhomogeneous corrosion product layer developed on steel surface. This layer had a certain protective effect on the substrate.

In the Cl^- addition system, the R_{ct} value was always higher than that in natural seawater system within 0-192h, showing that with the addition of Cl^- the high concentration decreased the dissolved oxygen content and inhibited the corrosion. In the HCO_3^- addition system, the R_{ct} value was higher than natural seawater system within 0-96 h, and lower after 96h. It indicated that the corrosion was inhibited first and promoted later. It was almost the same in the case of SO_4^{2-} addition.

3.3 Polarization curve

Fig.6 shows the polarization curves of Q235 steel immersed in different solutions for 192h. C-View software was used to fit the polarization curve of Tafel region, and the electrochemical parameters were listed in Table 3. As is seen from Fig.6, the polarization curves showed anodic passivation in all the four systems, indicating that oxide film or corrosion product film produced on the metal surface. The film hindered the diffusion of ions and led to the decrease of corrosion current. With the increase of polarization degree, the anode dissolved continuously and the corrosion was aggravated.

Compared with the natural seawater system, the higher concentration of Cl^- inhibited the anode dissolution. While with the increase of immersion time, the corrosion potential declined and the corrosion current density increased. In the HCO_3^- addition system, with the increase of anodic polarization degree, the polarization curve showed an anodic activation dissolution process and the corrosion rate increased. The reduction reaction of HCO_3^- was controlled by the activation process. In

the SO_4^{2-} addition system, The Tafel slope of anodic polarization curve showed obvious passivation characteristics. With the increase of anodic polarization degree, cracks occurred on the product film and the anodic dissolution rate increased. During the process of immersion, the degree of active dissolution of the electrode surface increased continuously, and the anodic polarization curve presented a typical transition from passivation to activation.

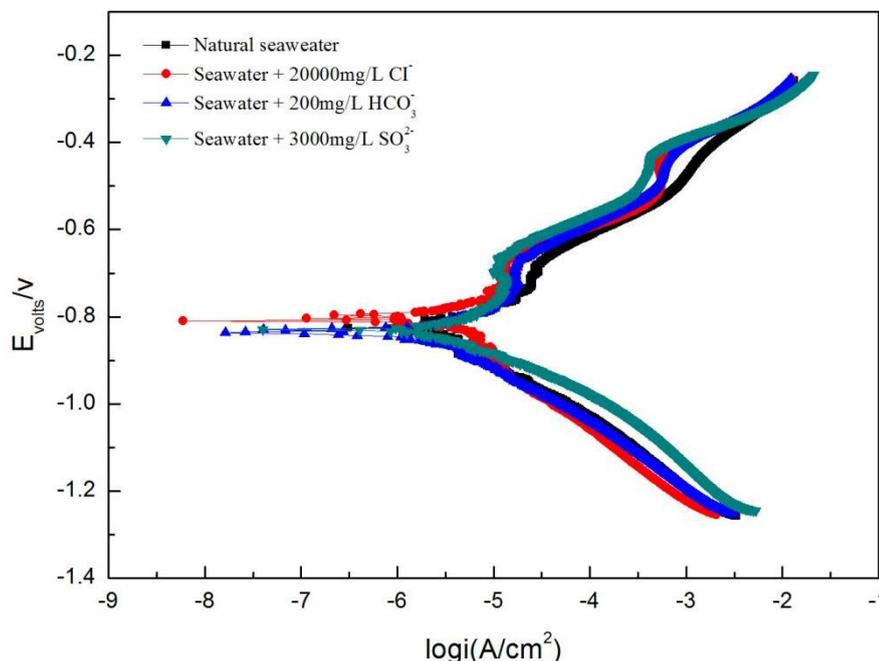


Figure 6. Polarization curves of Q235 steel immersed in different solutions for 192h

Table 3. Fitting values of Tafel polarization curves of Q235 steel immersed in different solutions for 192 hours

Condition	E_{corr} (V,vs.SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a ($\text{mV}\cdot\text{dec}^{-1}$)	β_c ($\text{mV}\cdot\text{dec}^{-1}$)
Natural seawater	-0.811	1.640	105	108
Seawater+20000mg/L Cl^-	-0.782	1.435	122	137
Seawater+200mg/L HCO_3^-	-0.821	3.644	180	160
Seawater+3000mg/L SO_4^{2-}	-0.827	7.219	452	139

From the fitting results of polarization curves in Table 3, it can be seen that compared with the the E_{corr} of Q235 steel in natural seawater system, -0.811V, and I_{corr} , $1.640 \mu\text{A}\cdot\text{cm}^{-2}$, the potential had a positive shift to -0.782V with addition of Cl^- and the corrosion current density declined to $1.435 \mu\text{A}\cdot\text{cm}^{-2}$. The potential shifted negatively to -0.821V, and the corrosion current density reached $3.644 \mu\text{A}\cdot\text{cm}^{-2}$ with addition of HCO_3^- . The potential shifted negatively in the SO_4^{2-} addition system, and the maximum corrosion current density was $7.219 \mu\text{A}\cdot\text{cm}^{-2}$. At this time, the corrosion rate was much higher than that in the natural seawater. This is consistent with the EIS results discussed above.

3.4 Surface morphology

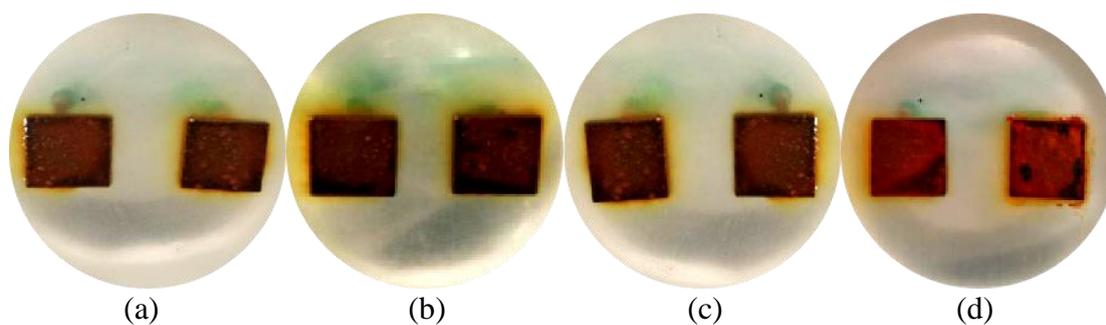


Figure 7. Corrosion morphology of Q235 steel immersed in (a) seawater (b) seawater + 20000mg/L Cl^- (c) seawater + 200mg/L HCO_3^- (d) seawater + 3000mg/L SO_4^{2-} solutions after 192h

As shown in Fig.7, the corrosion morphology of Q235 steel immersed in four solutions after 192h was observed. The surface of Q235 steel was subjected to different degree of corrosion with different characteristics. A large number of red-brown corrosion products were formed on the surface of the samples, and many corrosion spots occurred due to the localized corrosion. In the four systems, the corrosion products on the steel surface with Cl^- addition were relatively less, while in the solution system with HCO_3^- and SO_4^{2-} addition, the corrosion products were obviously more than that in natural seawater system. This indicated that the corrosion of was promoted at the concentration.

3.5 Discussion

It was reported that the effect of anions on corrosion of steel was related to the type and concentration of anions and the immersion time[18-20]. Under the same conditions, high concentration of anions would inhibit the corrosion due to the reduction of dissolved oxygen in solution caused by the high-concentration-anion and the inhibition of the reaction rate resulted. While low concentration of anions would promote the corrosion because the addition of anions led to the change of pH value, which destroyed the oxide layer on the substrate and accelerated the corrosion process.

In this work, the corrosion of Q235 steel was inhibited in the Cl^- addition system, while in the HCO_3^- and SO_4^{2-} addition system, it was inhibited firstly and then promoted in the later stage of the experiment. Research of Xue[21] showed that the corrosion resistance of Q235 steel decreased with the concentration when the Cl^- concentration was relatively low. As Cl^- was easily adsorbed on the electrode surface, which promoted the peeling of oxide film on the surface, then it penetrated into the substrate and promoted the corrosion. However, when the Cl^- concentration reached a certain value, the system presented obvious capacitance characteristics. The penetration of Cl^- into metal could be delayed or prevented, thus increasing the corrosion resistance. In addition, the high concentration of Cl^- led to the decrease of dissolved oxygen in solution, so the corrosion resistance also increased.

When the concentration of HCO_3^- was relatively low, the impedance would decrease slightly with the concentration, and the corrosion resistance of steel decreased continuously. When the

concentration of SO_4^{2-} was low, with the increase of concentration, it presented a transition from passivation to activation. The corrosion current density of steel increased with the increase of concentration and immersion time. As the thickness of oxide layer decreased, the corrosion resistance of the steel decreased and the corrosion was aggravated. A high concentration of SO_4^{2-} would keep the steel in a passivation state[22-24].

The above research showed that the anions contained in industrial wastewater (such as Cl^- , HCO_3^- , SO_4^{2-}) had a great influence on the corrosion behavior of port facilities, which would reduce the corrosion resistance and the service life of facilities. Therefore, it is very important to strengthen the management of port facilities. In view of the discharge of industrial wastewater, the concentration of ions should be controlled to prevent their damage to port facilities. Although some ions (such as high concentration Cl^-) would not reduce the corrosion resistance of facilities, the content should also be controlled in case of causing other hazards. According to the discharge standard of industrial wastewater, Cl^- should not be higher than 500 mg/L and SO_4^{2-} should not be higher than 600 mg/L. Generally, HCO_3^- would not exist alone in industrial wastewater, but the concentration should also be appropriate.

4. CONCLUSION

The corrosion behavior of Q235 steel in three anions at certain concentrations were studied by electrochemical methods such as open circuit potential(E_{ocp}), AC impedance spectroscopy and potentiodynamic polarization curve. The main conclusions are as follows:

During the whole experiment, the corrosion rate of Q235 steel firstly increased continuously in all solutions. A layer of corrosion products then developed on the surface of the steel, which had a certain protective effect on the substrate. Compared with the natural seawater system, the dissolved oxygen was reduced with addition of Cl^- in the seawater system, and high concentration of Cl^- inhibited the corrosion of the steel. The corrosion of Q235 steel was inhibited first and then promoted with the increase of immersion time in HCO_3^- and SO_4^{2-} addition systems due to the change of oxide thickness and passivation state on the metal surface.

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