Biocorrosion induced by Sulfate-Reducing Bacteria on Stainless Steel – A Preliminary Study

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ABSTRACT

304 stainless steel was tested under the media without Sulfate-reducing bacteria (SRB) and with SRB. The corrosion behaviors of 304 stainless steel in SRB and without SRB medium were studied by measuring the open circuit potential, the polarization curves and electrochemical impedance Spectrum , weight loss measurements to get the changes of fore-and-aft corrosion fouling. The open circuit potential shifted negatively with the time. The result showed that the slope of cathodic polarization curves measured in the medium included with SRB is lower than the one obtained in the medium without bacteria , while the slope of anodic polarization curves is higher than it. It is concluded that the process of anode polarization was repressed at the presence of SRB. With the growth of the culture time , the value of electrochemical impedance in the medium without bacteria reduced at first, then rose, while in the medium included with bacteria fell at all times. It indicated that SRB accelerated the corrosion of stainless steel. With the dipping time, a biofilm, under which corrosion products congregate to form local battery corrosion, was formed on the surface of stainless steel, so that the serious pitting corrosion is induced.

Keywords: sulfate-reducing bacteria; microbiologically influenced corrosion; polarization; electrochemical impedance spectrum

INTRODUCTION

Microbiologically influenced corrosion is the most common in natural aqueous environment, accounting for about 20% of corrosion [1]. The corrosion [2] which is caused or promoted by participation of microorganisms is known as microbiologically influenced corrosion (MIC). Microbiologically influenced corrosion represents one of the most serious forms of degradation in cooling water systems of many industries, as it is rapid and complex. In the cooling water of power plant, biofilms, which are composed of bacteria and theirs metabolic products, are formed on the surface of the condenser tube materials. When the biofilms exist on the metal tube materials' surface, pH values, dissolved oxygen concentration, the types of organism and stainless steel and their concentrations of the metal–biofilm interface are significantly different from the background solution. Biofilms formation on stainless steels have an indirect impact on the electrochemical of corrosion , causing an indirect increase in the corrosion rate ,the key lies in the interactions of the microorganisms on the metal surface and metal matrix [3].

It is considered that the corrosion damage is mostly caused by sulfate-reducing bacteria by the research and analysis. Sulfate-reducing bacteria(SRB) induced corrosion of carbon steel in a corrosive medium is a good example of the complex interactions and effects taking place among inorganic corrosion products and biofilms in a biologically conditioned interface. In the nature and industrial water systems, it is well known that sulfate-reducing bacteria propagate rapidly under anaerobic conditions [4]. Because of MIC had a significant impact on the economy and the environment; it has become a subject of extensive research in the recent 50 years [5].

With the stainless steel is widely applied in the industry, microbial corrosion of which is attracted more and more widespread attention [6]. Especially in the 1980s, Britain and the United States and other countries have set up a special microbiological corrosion research institutions, which focused on the electrochemical aspects of the anaerobic corrosion of iron such as stainless steel. Stainless steel has good corrosion resistance and good mechanical properties ,which is commonly used in the important parts, but under the influence of microorganisms, corrosion often occur in the weld and heat affected zone [7],thus limiting the scope of its application, therefore, it has great significance of further in-depth study on microbial corrosion of stainless steel and exploration.

Experimental principles
1 Principle of Corrosion weight loss

Weight loss method is a method to measure the corrosion rate based on the weight change of specimen before and after the corrosion , Weight loss rate v (g/cm^2·h) can be calculated according to the formula (1).

$$v_{-w} = \frac{W_0 - W_1}{At} \tag{1}$$

where ,

A: Experimental area, m^2;

t: Experimental cycle , h;

w_0 : Original sample weight, g;

w_1 : The specimen does not contain the weight of corrosion products after the experiment, g.

Where: $A = \dfrac{5 \times 2.5 \times 2}{1 \times 10^4} = 2.5 \times 10^{-3}$ (m^2)

t=24×21=504(h)

Because of metallic materials has a variety of different density, this Corrosion rate should not be the representative of corrosion depth of the loss, even the uniform corrosion. The average corrosion rate can be converted into the average erosion depth one units of time, (Corrosion rate, such as mm / a), the conversion formula is:

$$\nu_t = 8.76 \frac{\nu_{-w}}{\rho} \qquad (2)$$

Where:

ν_t : Corrosion rate, mm/a;

ν_{-w} : Corrosion weight loss rate, g / (m^2 • h);

ρ : Metal density, g/cm^3.

2 Principle of Electrochemical impedance spectrums

AC impedance spectroscopy method [8] is an electric signal measurement method which uses the small amplitude sinusoidal potential as the perturbation signal. As to the small amplitude signal infliction on the system, on the one hand big impact could be avoided; on the other hand the response to the disturbances could be linear approximation, which would make the mathematical treatment of the measurement results simple. At the same time, it is a frequency domain measurement method of impedance measurement over a wide range of frequency to study the electrode system, so it can get more information about the information structure of the electrode interface and the electrochemical kinetics than other conventional methods.

Experimental procedures

1 Experimental material

The material used for this investigation was 304 SS and had the chemical composition shown in Table 1.the size of the corrosion agravic sample is 50×25×2mm, the work surface area of the electrode for the electrochemistry test is 1cm^2. A wire was spot welded to one end of each electrode for electrical connection. The welded part was then embedded in epoxy resin for electrical isolation and firm attachment. The exposed surface of each rod was abraded to 1000#, and then the tip of each rod was treated in 20% nitric acid at 50°C for 30 min to prevent end-grain pitting.

Table 1 Composition of 304 SS

element	C	Si	Mn	Cr	Ni	Mo	Fe
Wt%	0.07	0.48	1.55	18.5	9.35	-	Bal

2 Cultivation of bacteria

The sulfate-reducing bacteria used in corrosion experiments were taken from the Songhua River water. APIRP-38 recommendatory medium was used, the basic components of which is as follows: Sodium lactate 3.5g/L, yeast extract 1.0g/L, vitamin C 0.25g/L, $MgSO_4$ ·7 H_2O 2.0g/L, K_2HPO_4 0.5g/L, NaCl 10.0g/L, $CaCl_2$ 0.1 g/L , NH_4Cl 1.0g/L, Na_2SO_4 0.5g/L, using NaOH adjust the p H value to 7.0 ~ 7.2, at 1.2×10^4 Pa vapor tension sterilize for 15 minutes, then add $FeSO_4$ • $(NH_4)_2 SO_4$ • 6 H_2O 0.2g by UV sterilization, sterilize in bactericidal pot for 20min, after cooling add it into the medium.

3 Corrosion and electrochemical method

Corrosion weight-loss method is performed under anaerobic conditions, the test pieces were separately immersed in enclosed container with SRB solution and without SRB solution, and then cultivate in the constant temperature box in (30±1 ℃) .Each group used three parallel specimens, continuously cultivate for 21d.

CHI660C electrochemical analyzer/ workstation was used as the electrochemical testing equipment. The experimentation adopted three-electrode system (Figure 1), reference electrode was saturated calomel electrode (SCE), auxiliary electrode was the platinum, and the working electrode is 304 stainless steel electrodes.
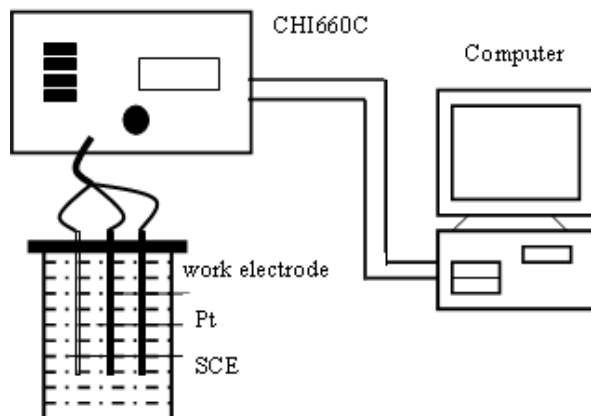

Fig. 1 Experimental equipment

After the working electrodes were sterilized, we divided them into two groups: one group was immersed in the medium with bacteria; another group was immersed in the medium without bacteria, for comparative trial. The open circuit potential was measured everyday. After the specimens were immersed in the medium for 1d, 2 d, 4d, 6d,8 d, impedance spectroscopy was separately measured. Measured frequency was 0.01 Hz ~10 kHz; measured signal was AC sine wave, of which amplitude was 5 mV. Polarization curves were measured just when the samples were immersed in medium after 8d, scanning the range from -1.4 V ~ 0.4 V, scanning speed was 1mV/s. All the experiments were carried out at room temperature (21±3°C).

RESULTS and DISCUSSION

1 Corrosion weight loss experiment

Corrosion rate of the sample can be calculated using the formulas (1), (2), the results are shown in Table 2. As can be seen from the table, the corrosion rate of the sterile solution of hanging do not change over times, the corrosion rate of static hanging increased slightly with corrosion time, This shows that the existence of SRB has accelerated the corrosion of 304 stainless steel.

Table 2 The weight loss of 304 stainless steel in culture inoculated SRB and without SRB

medium experimental parameter	Without SRB	With SRB
Weight loss (g/m^2)	0.9281	2.4481
v_{-w} (g/m^2·h)	0.7366	1.9429
v_t (mm/a)	0.0082	0.0217

2 Open circuit potential of electrodes

The open circuit potential of stainless steel electrodes is measured in the bacterium at different incubation time (0, 2,3,4,5,6,7,9,11,14 days). Table 3 is the open circuit potential for the 304 stainless steel electrodes measured under the two experiments. The SRB culture growth in airtight container can be divided into four stages: incubation period, rapid growth, stability, growth and decay period. From the SRB vaccination, with time increases, the number and activity of bacteria have changed ,the solution composition changes accordingly, so electrochemical behavior of stainless steel electrodes are also different. Studies have shown that [9], in the medium of malnutrition, the metal surface provide a good living conditions for bacterial growth, bacteria and their metabolites adsorbed to the solid surface, thus to form a microbial membrane, this dense bio-film provide a certain degree of mechanical barrier for electrode, play a role in physical protection; metabolic processes consumes sulfate and other substances which could inhibit corrosion of metal material, and results in metabolite such as corrosive sulfur ions, thus increases the corrosive of solution, in addition, many extra cellular polymer produced by bacteria secrete were acid and contain many functional groups[10], and it is easy combined with metal ions in the solution, also can accelerate the corrosion of metals. The above factors affect the electrochemical corrosion behavior of electrode.

The open circuit potential curves of 304 stainless steel electrode were shown in figure 2. In both media, the corrosion has experienced the phenomenon of negative movement from the corrosion potential since the early corrosion period, until after the first 7 days the shift become slow and eventually stabilize. However, just when immersed in medium, the open circuit potential of stainless steel in sterile medium are positively moving fast, the open circuit potential of stainless steel in bacterium medium is firstly experienced rapid negative shift then positive shift,

this indicates that the initial corrosion metabolic activities of bacteria reduce the concentration of oxygen in the surface of 304 stainless steel, suppress the formation of surface passive film, and had a major impact on its surface.

As shown in figure 2, the open circuit potential of stainless steel electrode in the bacteria solution is at the most in the first four days. In 4-6 days, SRB growth is in a stable growth period, the rapid metabolism of bacteria increased the corrosive of the solution, so that the open circuit potential shifted negatively during this period; In 7-9 days, SRB growth is in the attenuation period, the number and activity of bacteria gradually decrease, the corrosive effect of the electrode become weakening, so the open circuit potential changes marginally in this stage . In addition, the open circuit potential of the stainless steel electrode under bacteria environment is bigger than the open circuit potential of the stainless steel electrode under the sterile environment. This shows that, in the case of the bacterial content, the formation of bio-film plays a role of the corrosion resistance.
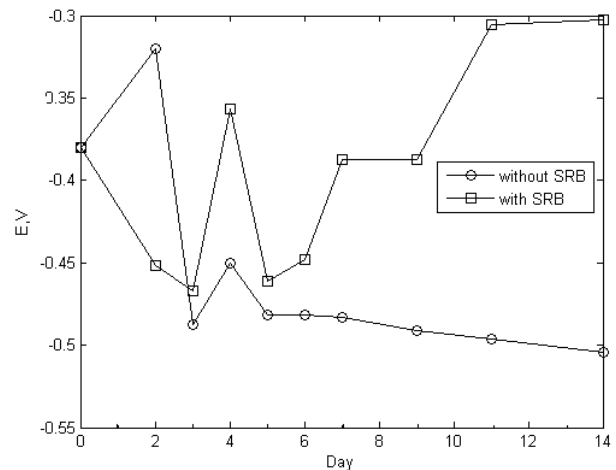

Fig. 2 open circuit potential of electrodes at different culture time in different mediums

3 Polarization curve

The polarization curves of 304 stainless steel electrodes after 8 d immersion in the medium with bacteria and without SRB (Figure 3) shows the cathodic polarization curves of them are basically the same shape, indicating that the existence of bacteria in the medium does not change the nature of cathode electrode process. the polarization curve under the conditions of bacteria shows more obviously oscillations at the vicinity of corrosion potential, which to some extent reflects that the growth of bacteria on the substrate metal surface affected the film-forming process, whereas the corrosion current density of stainless steel with bacteria in medium significantly greater than the sterile medium, and this also shows that the existence of SRB has accelerated the corrosion of 304 stainless steel.
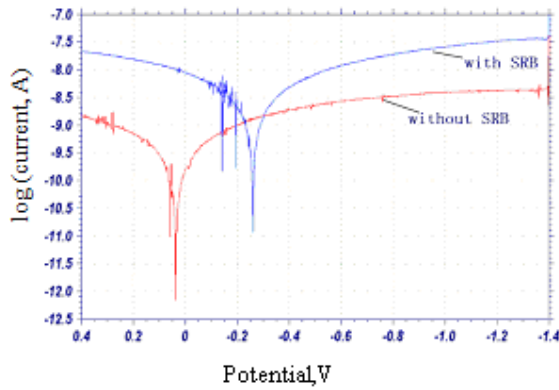
Fig.3 Polarization behavior of 304 stainless steel electrode after 8d immersion in different mediums

4 Electrochemical impedance spectrums

In a simple activation of the corrosion control system, when the solution resistance Rs between the reference electrode and the work electrode of can not be ignored, the equivalent circuit of the work electrode can be simplified for the polarization resistance Rp and the double-layer capacitance Cd in parallel connection, with Rs connected in series circuit. At this time, the impedance of electrodes is

$$Z = R_S + \frac{1}{\frac{1}{R_P} + jwC_d} \qquad (3)$$

By the mathematical treatment, formula (3) can be transformed to formula (4)

$$[z' - (R_S + \frac{1}{R_P})]^2 + (z'')^2 = (\frac{R_P}{2})^2 \qquad (4)$$

This is a circinal equation, of which radius is1/2Rp, coordinate of the center of the circle is (Rs + 1/2Rp, 0). With the real part Z' as the horizontal axis, the imaginary part Z" as the vertical axis, constructing under different measured frequencies of data mapping, a negative impedance spectroscopy can be get, Rs and Rp can be obtained[11]. According to EIS technology, when neglected concentration polarization, the Faraday impedance is the charge transfer impedance resistance Rt, it reflects the corrosion rate. Because the value of the sine wave imposed in the experiment is very small, the polarization control system activation Rt equal to the polarization resistance Rp. From the Stern-Geary equation [11], we can see the metal corrosion rate is inversely proportional to its polarization resistance.

The simulation method of AC impedance data are mainly equivalent circuit method, the geometric model (such as the brick layer model) and effective medium model, currently, the most used method is equivalent circuit model. In practice, often use different frequencies of small amplitude signals on some substances or systems and measure their electrical response. The advantages of the equivalent circuit are intuitive, easy to describe the electrical response in

frequency domain accurately, and can be associated with the physical parameters of the system.
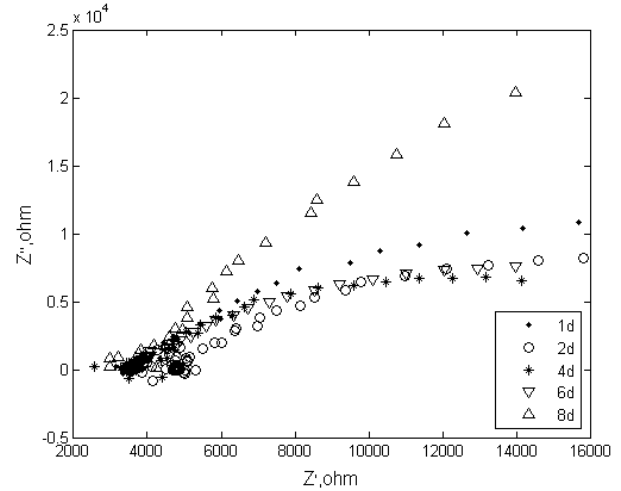

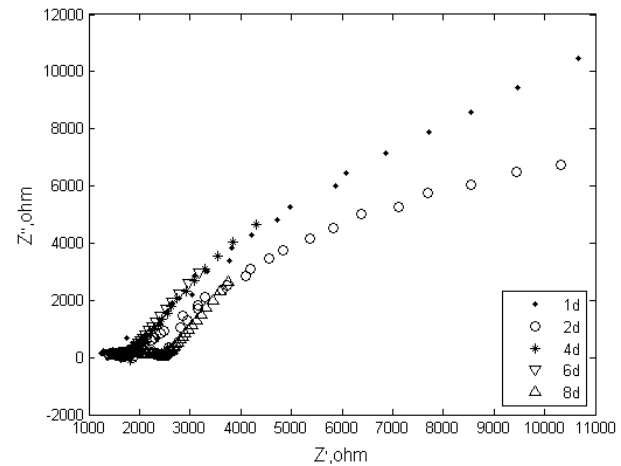Fig.4 EIS of 304stainless steel exposed to medium without SRB for different times

Fig.5 EIS of 304stainless steel exposed to medium with SRB for different time
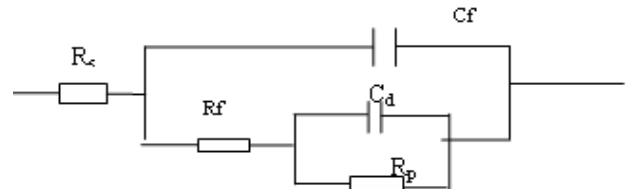

Fig.6 equivalent circuit of the 304 stainless steel electrodes in medium

In this paper, the electrochemical impedance spectrums of the 304 stainless steel electrode in medium with bacteria and without bacteria are respectively showed by figures 4 and 5. The curve of figures 4 and 5 can be similarly seen as a part of the semicircle. In bacteria solution, with the increasing of culture time, the "radius" of the impedance curve gradually decreased. If this curve is extended to the semi-axis, the "diameter" in the real axis can be seen as Z', that is, transmission resistance, while the high of the semicircle can be seen as a mode of Z". So, the equivalent

circuit was created which is shown in Figure 6. EIS are analyzed with the equivalent circuit. There into, Rs is the solution resistance, Rp is the polarization resistance, Cd is the double-layer capacitance. Rf is the membrane resistance, Cf is the membrane capacitance. Software ZsimWin was used for fitting analysis. Figure 7 and Figure 8 shows a good effect.

Stainless steel immersed in medium without SRB after 2d, the surface polarization resistance Rp is12.26kΩ, 4 d later the Rp reduced to10.97 kΩ, 8 d later Rp rose to 50.03 kΩ, however, After 2d of immersion in medium with SRB, the surface polarization resistance Rp is10.84 kΩ, 4 d later the Rp descend to 10.60kΩ, 8 d later the Rp declined to 0.3545kΩ. Rp variation is shown in figures 3 and 4. It is seen sterile stainless steel electrode at medium impedance values decreased at first, then rise, which is because a number of corrosive ions in the medium promote the stainless steel corrosion resistance to drop, along with the corrosion reaction ongoing and solution of oxygen have

been restored, gradually compact passive film is formed on the stainless steel surface (mainly Fe oxides and hydroxides)[12], thus its polarization resistance is corresponding large. While in the medium included with bacteria, stainless steel electrode impedance values decreased significantly at all times. It indicated that SRB accelerated the corrosion of stainless steel.

Table 3 variation of Rp

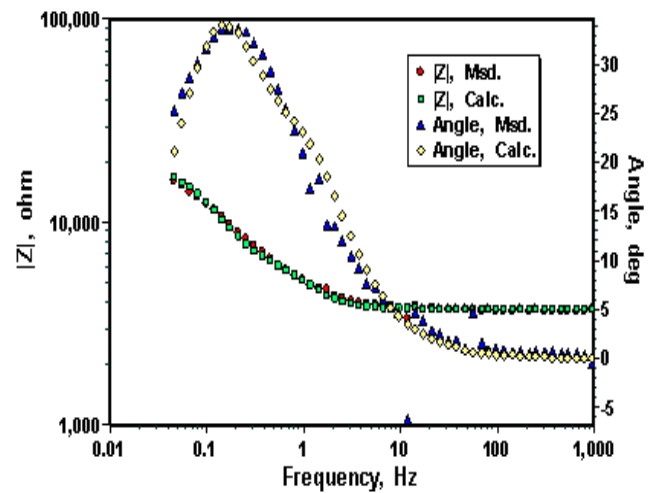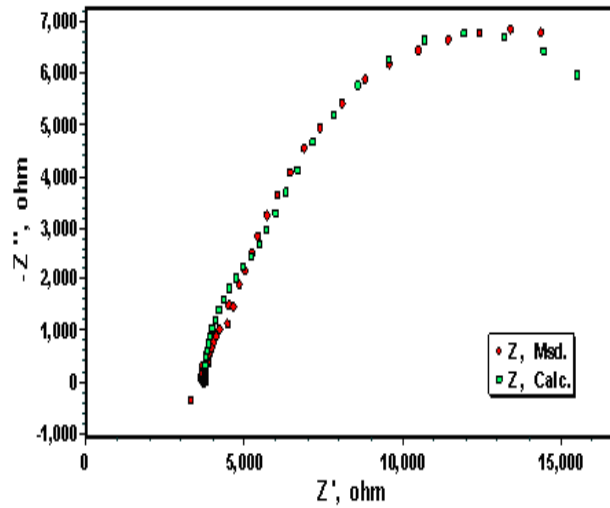| time	Rp(kΩ)	Without SRB	With SRB
1d		15.87	17.28
2d		12.26	10.84
4d		10.97	10.60
6d		11.81	7.992
8d		50.03	0.3545

Fig 7 the fitting result of 304stainless steel exposed to medium without SRB for 6d (left,Nyquist plots;right,Bode plots)
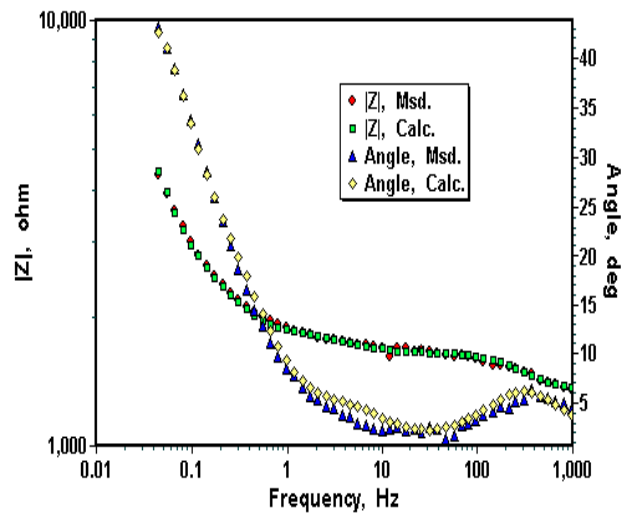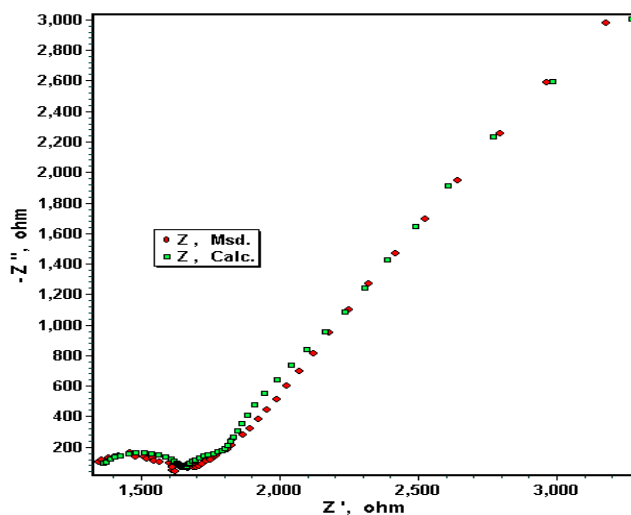

Fig 8 the fitting result of 304stainless steel exposed to medium with SRB for 6d (left,nyquist plots;right,Bode plots)

CONCLUSIONS

1. Electrochemical experimental results show that the existence of SRB has a certain extent accelerated the corrosion of 304 stainless steel.

2. Just immersed in the medium, the bacteria significantly accelerated the corrosion of 304 stainless steel. Changes of the open circuit potential are different under with SRB and without SRB conditions, which are related to the structure of electrode surface biofilm, metabolic products of bacterial growth and the change of PH value of solution [14]. It shows that the existence of SRB inhibited the formation of passive film of stainless steel and accelerated the corrosion of 304 stainless steel.

3. Polarization curves and electrochemical impedance spectroscopy studies have shown that the existence of bacteria did not change the nature of the process the cathode electrode, but to make stainless steel to reduce the polarization resistance, which reduces the corrosion resistance of stainless steel.

NOMENCLATURE

A Experimental area, m^2

t Experimental cycle , h

w_0 Original sample weight, g

w_1 The specimen does not contain the weight of corrosion products after the experiment, g

v_t Corrosion rate, mm/a

v_{-w} Corrosion weight loss rate, g / (m^2 • h)

Rs the solution resistance, Ω

Rp the polarization resistance, Ω

Cd the double-layer capacitance, Ω

ρ Metal density, g/cm^3

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