Electrochemical techniques for determining corrosion rate of rusted steel in seawater

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Corrosion rates of mild steel for long-term immersion were estimated by electrochemical and weight-loss methods. The results showed that application of electrochemical methods yielded erroneous values. The main reason was that, β-FeOOH, produced after long-term immersion with high electrochemical activity in the inner rust layer, exerted significant influence. In electrochemical tests, even small polarization can make β-FeOOH participate in cathodic reaction, which leads to overestimating corrosion rate. In order to confirm it, electrochemical behaviour was studied in aerated and deaerated conditions to investigate the effect of rust layers on reduction reaction. After calibration, the electrochemical measurement result was coincided with the weight loss.

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1. Introduction

Mild steel is the major material used for infrastructures in marine environments. It predominates in structural steel applications including ship hulls, offshore platforms, sheet piling and coastal facilities. Its general or uniform corrosion is the most important form of corrosion and is of considerable economic importance. World-wide there is increasing attention being given to reliable methods for measuring corrosion rate. Weight-loss measurement is currently the most direct and reliable method but time consuming and information limited. Electrochemical measurement, which tests faster with more information, and can be used in field detection combined with other methods, is a non-destructive, quantitative technique and a powerful tool for researching corrosion process.

But there are difficulties in studying corrosion behaviour of complex system such as rust/metal system by electrochemical measurement because the existence of rust complicates the electrochemical corrosion process. Electrochemical reactions under rust are not any more simple reactions including metal anodic dissolution and oxygen cathodic reduction but complex corrosion process combined of multiple sub-processes involving rust redox reactions, mass transportation though rust, electric charges movement between interfaces, microorganism propagation in porous rust and some other complex corrosion processes [1–3], which make metrical corrosion rates different between electrochemical and weight-loss measurements [4].

Electrochemical reactions are obviously consistent with the compositions of the rust layers and the compositions are not the same in different environments. The phase compositions of the corrosion products in an aqueous medium depend on different parameters, such as temperature, pH and the oxygen content. The presence of various ions in aqueous solution may also affect the phase compositions of the corrosion products. Refait [5] analyzed the rust layers formed on steel piles immersed during 25 years in the Bay of Brest, at Sainte Anne du Portzic by Raman spectroscopy and scanning electron microscopy. He found the rust layers consisted of three main strata, the inner one mainly composed of magnetite, the intermediate one of iron (III) oxyhydroxides and the outer one of hydroxysulfate green rust GR (SO4

Different compositions have different physical and chemical properties. In some cases, they can transform to others. Magnetite generally has been found at the metal/rust interface of thick rust
layers [8,9]. According to Evans' model, the anodic oxidation of iron is balanced by the cathodic reduction of the first formed ferric rust to magnetite under wet conditions when access of oxygen is limited [10,11]. Continuous wetting can stabilize the magnetite phase [12]. The ferric oxyhydroxide of $\alpha$-FeOOH is the final stable corrosion product, which is altered from $\gamma$-FeOOH, via amorphous substance, to final state after long-term exposure [13]. Mucic et al. [14] proposed that the first step of the corrosion process of steel in a marine environment was the formation of FeCl$_3$, which further transformed to $\beta$-FeOOH by slow hydrolysis. Misawa et al. [15] reported that $\beta$-FeOOH could be obtained by the dry aerial oxidation of $\beta$-Fe$_2$(OH)$_3$Cl which precipitated from slightly acidic solutions of ferrous chloride at room temperature.

Because some compositions such as $\beta$-FeOOH and $\gamma$-FeOOH are reducible, the corrosion process will change. Feliu et al. [16] reported that the presence or absence of dissolved oxygen in the saline medium had no influence on the response of rusted steel to the electrical signals applied since rust itself provided the cathodic reaction involved in the corrosion of the steel substrate. Hoffmann and Stratmann [17] considered that if the transport of oxygen was slow, the reduction of the oxide scale was possible when he studied the corrosion of rusted iron coated by organic lacquers. The redox of rust makes corrosion process more complex.

Since both the marine environment and rust/metal system were complex, researchers mostly studied metallic corrosion by estimating the material losses exposed in actual marine field for long term. Hudson and Stanners [18,19] reported data collected after 2 and 5 years of exposure. Forgson et al. [20] reported data collected in the Panama Canal Zone for exposures to 16 years. Melchers [21–23] proposed a multi-phase phenomenological corrosion loss-time model to describe the marine corrosion behaviour for mild and low alloy steels. ASTM of US commissioned LaQue corrosion test centers to carry out field trials of various materials in 14 different actual marine fields of the world [24]. It provided a basis for evaluating the worldwide marine corrosion.

In addition to weight-loss measurement, some researches about rusted steel were also performed by electrochemical measurement. Feliu et al. [16,25] studied atmospherically rusted specimens with electrochemical impedance spectroscopy (EIS). The results showed that the shape in the impedance diagrams seemed to be markedly influenced by diffusion processes in the rust layer and/or by the porous nature of the rusted steel electrode. Since the majority of the Nyquist diagrams obtained with the rusted steel deviated from the typical semicircular form, it was not clear how kinetic information could be obtained from these diagrams. It therefore seemed preferable to use the d.c. data for the electrochemical determination of the corrosion rate for rusted steel [26]. But in investigation, they [27] also discovered that anomalously large differences between values of the polarization resistance ($R_p$) measured in the time and frequency domains posed a serious problem because the measurements were made under conditions far from the steady state. For this reason, selection of suitable scanning rate for d.c. test is significant.

In recent years, some researchers also observed that important deviation existed when estimating the corrosion rate of the rusted mild steel by electrochemical measurement because electrochemical signal could work on corrosion product [28,29]. Andrade et al. [30] confirmed that $R_p$ measured in $-0.7$ V versus SCE were highly influenced by several redox processes that led to overestimation of the rebar corrosion rate by investing electrochemical behaviour of steel rebars with EIS. González et al. [4] proved that traditional polarization resistance method was not suitable for determining corrosion current density of rusted steel. The presence of 2-valent/3-valent iron in the rust could cause high pseudocapacitance values associated with redox reactions in the solid phase. The rust favoured corrosion both by providing a reducible material for the cathodic reaction and by acting as a porous electrode for the reduction of oxygen. Videm [31] showed that different electrochemical methods gave a large divergence in linear polarization ($R_p$) resistance when measuring corrosion rate for steel exposed to alkaline solutions by cyclic voltammetry, potentiostatic exposure, potentiostatic pulses, galvanostatic pulses and EIS. The dominating reason was that redox reactions of the corrosion product could consume a part of current, which decreased the polarization resistance and increased the corrosion rate.

In order to develop reliable detection and monitoring electrochemical techniques for researching long-term corrosion behaviour of rusted steel, this paper systematically studies the discrepancies between electrochemical and weight-loss results, analyzed the reasons and offered the calibration method.

2. Experimental

2.1. Materials preparation

Total immersion tests were performed on mild steel (Q235), coupons of dimensions $50 \times 25 \times 3$ mm for weight-loss measurement with a hole for 5 mm in diameter located in the top middle and 10 mm in diameter embedded in epoxy resin for electrochemical measurement. The steel compositions are given in Table 1. The specimens were polished to 800 grit, cleaned ultrasonically in acetone and rinsed with distilled water. All the specimens were immersed synchronously in chest filled with seawater in laboratory conditions. Seawater for tests was from Huiquan Bay of Qingdao, filtrated before tests, static in the chest and replaced every week. The indoor average temperature was 20°C. The test commenced on November 2007. The corrosion rates of coupons were measured periodically by weight-loss and electrochemical measurements. Triplicate recoveries were made every time for weight-loss measurement and averages were obtained.

The coupons immersed in seawater for different periods were taken out from the chest for weight-loss measurement. The rust layers were scraped off from the steel surface with keeping the steel substrate intact by a surgical blade, and residual rust on steel was removed by immersion in a mixed solution composed of 500 ml hydrochloric acid + 20 g hexamethylenetetramine + 1 L distilled water. After corrosion products had been completely removed, the specimens were rinsed with distilled water, dried with blower, and then weighed to determine their mass loss.

2.2. Analysis of composition and structure for rusted steel

Infrared spectra (IR) were obtained from a Nexus-380 infrared spectrophotometer with 32 scans in the ranges 400 and 1300 cm$^{-1}$ with the accuracy of 4 cm$^{-1}$. The outer rust layers were scraped off using a coarse wire brush and inner layers by a surgical blade. The rust products were grounded into fine powder and pressed to pellets with appropriate amount of KBr. Cross-sections of the surface for corrosion products were observed by J-T21821 color video camera.

2.3. Electrochemical measurements

Electrochemical measurement was implemented with a PAR-STAT 2263 potentiostat/galvanostat electrochemical system

<table>
<thead>
<tr>
<th>Table 1 Chemical compositions in wt.% of Q235 mild steel.</th>
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<tr>
<td>Chemical composition</td>
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<tr>
<td>Mass%</td>
</tr>
</tbody>
</table>
equipped with Powersuite software. The electrochemical tests in seawater were carried out using three-electrode cell system. The working electrode was mild steel specimen. Platinum foil and a saturated calomel electrode served as the auxiliary and reference electrodes, respectively. The system was in a good ventilation to keep the concentration of oxygen balance between the electrolyte and atmosphere in aerated electrochemical tests. In deaerated electrochemical tests, the schemes of the electrochemical cells could be seen from Fig. 1, the solution was deoxygenated with nitrogen of high purity before tests for 4 h while the flow of the gas in the solution was continued during the measurements. The bubbling rate, which was not measured, was small and the same which could be ignored in all the experiments. The linear polarization curves were obtained in the potential range \(-10\) to \(+10\) mV (vs. \(E_{\text{corr}}\)) with a scan rate of 0.1 mV/s, which could make the measurement under the steady state conditions. To avoid the influence of the rust layers, the potentiodynamic polarization curves were made from \(E_{\text{corr}}\) to cathode, after stabilization, from \(E_{\text{corr}}\) to anode with a scan rate of 0.1 mV/s. The data were analyzed with CView2. Three parallel specimens were performed for polarization curves and representative results were selected. The same five parallel specimens were carried out every time for linear polarization measurement and representative results were also selected.

3. Results and discussion

3.1. Weight-loss experiments

At present, weight-loss measurement is the most accurate and precise method for determining metal corrosion rate because the experimentation is easy to replicate and, although long exposure times may be involved, the relatively simple procedure reduces the propensity to introduce systematic errors.

Fig. 2(a) shows corrosion loss of weight-loss measurement as a function of time. Fig. 2(b) shows the variation of instantaneous corrosion rate with increasing period of exposure (the slope of the curve in Fig. 2(a)). The conversion of gravimetric parameters into electrochemical ones is made by means of Faraday’s law:

\[
\dot{i}_{\text{corr}} = \frac{nFAm}{MtA} \tag{1}
\]

where \(\dot{i}_{\text{corr}}\) is current density in A/cm² which stands for corrosion rate, \(Am\) is weight loss due to corrosion in g, \(n\) is valence, \(F\) is Faraday’s constant (56,500 coulombs), \(M\) is molecular weight of metal in g/mol, \(t\) is time in s, \(A\) is the area of metallic surface exposed to the corrosion in cm².

From Fig. 2(b), it is observed that there is a period (about 12 weeks) during which there is initially a very high corrosion rate followed by a steady decline. This trend agrees to the results invested by other experts [21].

3.2. Polarization curves behaviour

Electrochemical measurement is considered to be a fast and efficient method which reflects the transient electrochemical process, so it can be used for measuring corrosion rate on-site. The use of polarization curve is very limited due to its destructive nature. However, it has to be stressed because from the shape of the experimental curve it may be possible to obtain important information on the kinetics of the corrosion reactions. Fig. 3 shows the polarization curves of rusted steels immersed in seawater for various exposure periods. With increasing of immersion time, the corrosion potential \(E_{\text{corr}}\) shifted to a positive value and almost unchanged. The shape of the anodic portion and anodic reaction rate basically unchanged, which indicated that the rust had little effect on anodic process. The most common anodic reaction was active iron dissolution. However, the shape of cathodic portion changed greatly with the influence of the rust layers. The cathodic behaviour had almost the same performances before 8 weeks’ immersion, in contrast, after 8 weeks’ immersion, cathodic limiting current flat and cathodic reaction rate increased gradually. The corrosion process of mild steel was controlled by cathodic process in
seawater, so the corrosion rate increased gradually with growth of rust layers, which was different from the result of weight-loss.

3.3. Comparison of corrosion rates for long-term exposure between electrochemical and weight-loss results

Linear polarization resistance technique (LPR) is a conventional electrochemical method for determining corrosion rate. It is considered to be a fast and non-destructive technique because the measurement conditions are near the steady state and the results are close to the truth. As a result, it is widely applied to study rebar corrosion [32,33].

Fig. 4 shows the linear polarization curves of rusted steel immersed in seawater for various periods. It was observed that the results could be divided into three parts:

- The fitted zone was chosen in the linear region (from –5 to +5 mV vs. Ecorr).
- 8 weeks' immersion, and it reduced slightly to 23 mV/dec from 8 to 12 weeks, then it was 19 mV/dec and never changed. Actually, the accurate B value is not easy to determine, but it will not change the trend of corrosion rate with increasing of exposure time.
- After calculation, the B value was 26 mV/dec before 8 weeks' immersion, and it reduced slightly to 23 mV/dec from 8 to 12 weeks, then it was 19 mV/dec and never changed. Actually, the accurate B value is not easy to determine, but it will not change the trend of corrosion rate with increasing of exposure time.

The values of Rcorr estimated by substituting B into Stern-Geary equation, which is expressed as

$$i_{corr} = \frac{B}{R_p}$$  (2)

$$B = \left\{ \left( \frac{\partial \ln I_a}{\partial \Delta E} \right)_{\Delta E=0} \right\} + \left\{ \left( \frac{\partial \ln I_c}{\partial \Delta E} \right)_{\Delta E=0} \right\}^{-1}$$  (3)

where B is not always a constant but should change following by the variety of corrosion behaviour [34]. $I_a$ and $I_c$ are anodic and cathodic density separately in $E$. $\Delta E$ is voltage step in V. In the experiment, it could be concluded that the anodic Tafel slopes of the polarization curves almost did not vary, while the cathodic Tafel slopes continually decreased with increasing of exposure time (Table 2). After calculation, the B value was 26 mV/dec before 8 weeks' immersion, and it reduced slightly to 23 mV/dec from 8 to 12 weeks, then it was 19 mV/dec and never changed. Actually, the accurate B value is not easy to determine, but it will not change the trend of corrosion rate with increasing of exposure time.

The values of $i_{corr}$ estimated by substituting B into Stern's formula, were compared to the results determined by weight-loss measurement in Fig. 6. Fig. 6(a) shows corrosion loss as a function of time which was obtained by integration after Faraday transformation. Fig. 6(b) shows the variation of instantaneous corrosion rate with increasing period of exposure. During the initial 8 weeks' immersion, both corrosion loss and instantaneous corrosion rate by LPR and weight-loss measurement had the same variations and values. The $i_{corr}$ values decreased gradually. After 8 weeks' immersion, different from the monotonic decline of corrosion loss data, $i_{corr}$ determined by LPR, turned to increasing which resulted in deviating from weight-loss result gradually. There is no doubt that the corrosion rate determined by weight-loss measurement is credible. The electrochemical measurement result before 8 weeks' immersion was in agreement with the weight-loss result, so it was credible, too. After 8 weeks' immersion, it was unreliable

<table>
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<tr>
<th>Time (week)</th>
<th>1 week</th>
<th>4 weeks</th>
<th>8 weeks</th>
<th>12 weeks</th>
<th>24 weeks</th>
<th>48 weeks</th>
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<tr>
<td>$b_a$(mV/dec)</td>
<td>77</td>
<td>75</td>
<td>72</td>
<td>70</td>
<td>64</td>
<td>62</td>
</tr>
<tr>
<td>$b_c$(mV/dec)</td>
<td>316</td>
<td>305</td>
<td>230</td>
<td>222</td>
<td>132</td>
<td>150</td>
</tr>
<tr>
<td>$R$(mV/dec)</td>
<td>26.8</td>
<td>26.1</td>
<td>23.8</td>
<td>23.1</td>
<td>18.7</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Table 2

Change of Tafel slopes for polarization curves with increasing of immersion time.


layer exposed for 18 weeks contained $\gamma$-FeOOH without any $\beta$-FeOOH, while that of the inner rust layer exposed for the same time contained not only $\gamma$-FeOOH but also a lot of $\beta$-FeOOH, which manifested in the intensity of $\beta$-FeOOH peak increasing. Besides of this, a peak appeared at 587 cm$^{-1}$ corresponded to Fe$_3$O$_4$.

3.6. The reasons of discrepancy between electrochemical and weight-loss results

For mild and low alloy steels, it is assumed that the corrosion product is uniform. It is also confirmed that the anaerobic activity could be ignored during 1 year’s immersion [21]. Thus, when the coupons were under steady state in electrochemical test, the electrochemical activity of rust layers may be the main reason for overestimating the electrochemical corrosion rate. For weight-loss measurement, cathodic corrosion reaction and anodic corrosion reaction are performed equivalently at corrosion potential. For electrochemical measurement, it needs to carry out cathodic and anodic polarization to some extent which leads to electrochemical corrosion reactions deviating from those at corrosion potential. This could cause electrochemical reactions different from those of non-polarization state, and even induce some reactions not available in equilibrium state, leading to the reactions in electrochemical test different from those of equilibrium state and overestimating corrosion rate. Therefore, the electrochemical activities of rust layers before and after 8 weeks’ exposure may be different. It was consistent with the discoveries of changes for compositions and structures before and after 8 weeks’ exposure.

The rust layer was loose during the initial immersion period, composed of $\gamma$-FeOOH and a small quantity of $\beta$-FeOOH. After a long-term immersion, the thicker inner layer contained a large amount of $\beta$-FeOOH appeared. Both $\beta$-FeOOH and $\gamma$-FeOOH are able to exhibit high reduction reactivity and $\gamma$-FeOOH is less reactive than $\beta$-FeOOH. When these two components coexist, $\beta$-FeOOH plays a major role in accelerating the corrosion rate [35, Lair [36] estimated reduction potentials of $\beta$-FeOOH and $\gamma$-FeOOH in different solutions. The results showed that the reduction potentials of $\beta$-FeOOH were $-$440 mV (vs. SHE) in 0.1 mol/l NaCl solutions with pH 8.5, while those of $\gamma$-FeOOH were $-$510 mV (vs. SHE). The order in reduction efficiency is $\beta$-FeOOH $>$ $\gamma$-FeOOH. The fact that $\gamma$-FeOOH is often observed along with goethite in rust scales [37,38] may also result from its limited reactivity with iron. In aerated corrosive media, the predominant oxidising species is oxygen and ferric products which are formed and accumulate within the corrosion layer. When the supply of oxygen is transport-limited, a galvanic coupling between iron and ferric product can occur, corresponding to an electron transfer from iron (anodic site) to ferric product (cathodic site). Hoerl et al. [39] studied the iron corrosion mechanisms occurring inside the rust layer during a wet–dry cycle. He suggested that the metal surface left in contact with electrolyte by the rust layer was, in one hand, very small and, in other hand, difficult of access by oxygen, which led $\gamma$-FeOOH being the primary oxidising species in wetting stage. When humidity was high, the rust layers had large moisture content, oxygen was easy to diffuse through rust layers and oxygen reduction reaction took place. Therefore, the difficulty of dissolved oxygen diffusion decides what kinds of reduction reaction occur.

During the initial immersion period, the main rust composition is $\gamma$-FeOOH. Dissolved oxygen transport is favoured through loose rust layer. In electrochemical tests, the reduction of $\gamma$-FeOOH may not be observed because of $\gamma$-FeOOH limited reactivity. The anodic and cathodic reactions progress as follow:

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

$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ \hspace{1cm} (5)
Cathodic reaction: \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (6) \]

For cathodic control, the corrosion rate is \[ i_{\text{corr}} = i_{\text{O}_2} \quad (7) \]

where \( i_{\text{O}_2} \) is current density of oxygen reduction in A/cm\(^2\). After long-term immersion, the main rust compositions are \( \gamma\)-FeOOH, \( \beta\)-FeOOH and Fe\(_3\)O\(_4\). Dissolved oxygen is almost depleted because the dense inner rust layer hinders oxygen diffusion. In electrochemical tests, a certain degree of electrochemical disturbance may cause \( \beta\)-FeOOH deoxidized for its high reduction efficiency.

Anodic reaction: \[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (4) \]
\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad (5) \]

Cathodic reaction: \[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (6) \]
\[ \text{Fe}^{2+} + 8\text{FeOOH} + 2e^- \rightarrow 3\text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (8) \]

Corrosion rate is \[ i_{\text{corr}} = i_{\text{O}_2} + i_{\text{rust}} \quad (9) \]

where \( i_{\text{corr}} \) is corrosion current density for rusted steel which stands for corrosion rate of rusted steel, \( i_{\text{rust}} \) is current density of rust reduction in A/cm\(^2\). For weight-loss measurement, cathodic corrosion reaction and anodic corrosion reaction are performed equivalently at steady corrosion potential (if not consider excursion). For electrochemical measurement, it needs to carry out cathodic and anodic polarization (at least 5 mV). When cathodic polarization, the anodic reaction will be weakened, while anodic polarization, the cathodic reaction will be weakened, too. The metal surface state is different with that of weight loss. The more important is that the reduction potential of \( \beta\)-FeOOH is slightly lower than corrosion potential. When weight-loss method is performed, the quantity of reduction is small, so it does not influence the corrosion reaction. For electrochemical measurement, it needs to carry out cathodic polarization. It is this process that strengthened the reduction of \( \beta\)-FeOOH (it is obvious in Fig. 3 that the cathodic current is remarkable enhanced), which increases the cathodic and corrosion currents, as a result, the electrochemical result deviates from the weight-loss. This is the difference between these two methods. From above analysis, it could be concluded that electrochemical and weight-loss measurements perform the same reactions during the initial immersion period, which exhibits the consistent results. After long-term immersion, the electrochemical measurement reflects the corrosion rate contains reduction current of rust layers in polarization process, which leads to overestimating the result.

3.7. Proportion of rust reduction in cathodic reaction

Because the corrosion current density contains rust reduction current after long-term immersion, the electrochemical estimates...
have systematically yielded higher values than the gravimetric corrosion loss. Theoretically, obtain the rust reduction current and deduct it, the rest divided by the electrode surface area corresponds to the real corrosion rate. Let the proportion between rust reduction current and total corrosion current be $\alpha$, the corrosion rate may be solved by Eq. (10).

$$I'_{\text{corr}} = i_{\text{a}_1} + i_{\text{rust}} = I_{\text{corr}} \times (1 - \alpha) + i_{\text{corr}} \times \alpha$$  \hspace{1cm} (10)$$

where $i_{\text{a}_1} = I_{\text{corr}} \times (1 - \alpha)$

In order to verify the above hypothesis is reasonable, linear polarization curves were performed in aerated and deaerated conditions separately. The values of $R_p$ (in aerated condition) and $R_p'$ (in deaerated condition) were summarised in Table 3.

In aerated condition: $i_{\text{corr}} = i_a = i_{\text{a}_1} + i_{\text{rust}} = \frac{B}{R_p}$  \hspace{1cm} (12)

where $i_a$ and $i_1$ are anodic and cathodic current density separately in aerated condition. $R_p$ actually reflects the combined action of oxygen and rust layer. After deoxygenating, only the rust layer is reduced, which was reflected by $R_p'$.

In deaerated condition: $i'_{\text{corr}} = i_1 = i_{\text{a}_1} = \frac{B}{R_p'}$  \hspace{1cm} (13)

where $i_{\text{a}_1}$ and $i_{\text{a}_1}'$ are anodic and cathodic current density separately in deaerated condition. For electrode reaction, the more materials are involved, the larger the electric quantity and current density for the same electrode surface area are, while the current density is inversely proportional to the polarization resistance. In aerated and deaerated conditions, the values of $B$ are almost same, the reciprocal ratio of polarization resistances can reflect the proportion of rust reduction current in corrosion (Eq. (14)).

$$\alpha = \frac{R_p}{R_p'} = \frac{1}{t}$$  \hspace{1cm} (14)

In aerated condition, $\alpha$ is the ideal proportion of rust reduction in cathodic process (Fig. 9(a)), and $1 - \alpha$ is the proportion of oxygen reduction (Fig. 9(b)). Fitting curve of Fig. 9(b), Eq. (15) can be produced.

$$1 - \alpha = 4.21446 - 3.55173t^{0.02559}$$  \hspace{1cm} (15)

where $t$ is exposure time in $d$. It can be confirmed that in electrochemical tests, the rust layers around the corrosion potential can participate in reduction reactions. With the rust layers thicker, it is difficult for oxygen to transport through, oxygen reduction proportion decreases and the rust layers' increases.

3.8. Calibration of electrochemical corrosion rate for rusted steel

According to Eq. (15), the values of oxygen reduction proportion can be obtained with increasing of immersion in electrochemical tests. Substitute them into Eq. (11), the current density of oxygen reduction could be calculated. This method can be used to calibrate the electrochemical measurement result.

The parameter $\alpha$ and $1 - \alpha$ were measured in deaerated condition. During the initial immersion period, part of rust layers participate in reduction reaction because $\gamma$-FeOOH can be reduced in deaerated condition. But in actual aerated condition, the rust layer is thinner and looser, dissolved oxygen can diffuse easily to the metal/rust interface. With ample oxygen, $\gamma$-FeOOH cannot be reduced. The reduction of oxygen is the major cathodic reaction in this stage without considering the reduction of rust layer. The measured result is the reduction current density of oxygen and also real corrosion rate.

As the inner rust layer grows in thickness, the supply of oxygen may gradually diminish, slowing down the rate of oxygen diffusion, and a large amount of $\beta$-FeOOH appears with higher electrochemical activity. Oxygen and rust layers participate in reduction reactions simultaneously during this period. The smaller dissolved oxygen content in metal/rust interface makes rust layers the major cathodic reduction materials. In this deaerated situation, the proportion of rust layers participated in the reduction reaction follows the variety of $\alpha$.

According to the above analysis, combined with the experimental data, during the exposure of the first 8 weeks, only oxygen reduction takes place, the electrochemical measurement result is

<table>
<thead>
<tr>
<th>$R_p$ ((\Omega \text{ cm}^2))</th>
<th>1 week</th>
<th>2 weeks</th>
<th>4 weeks</th>
<th>6 weeks</th>
<th>12 weeks</th>
<th>24 weeks</th>
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</table>

Fig 9. Proportion of rust reduction (a) and oxygen reduction (b) in cathodic process vs. exposure time.
4. Conclusion

(1) Electrochemical estimate coincided with mass-loss result during the initial immersion period while great deviations yielded after long-term immersion, which indicated that the data determined by electrochemical measurement was trustworthy in this period.

(2) The rust was loose during the initial immersion period, composed of $\gamma$-FeOOH and a small quantity of $\beta$-FeOOH. After long-term immersion, the inner layer contained a large amount of $\beta$-FeOOH with higher electrochemical activity appeared.

(3) For weight-loss measurement, the corrosion rate is connected with the rate of dissolved oxygen diffusion, which is inhibited by the gradual build-up of corrosion products. For electrochemical measurement, it is oxygen that participates in cathodic reduction reaction during the initial immersion period. After long-term immersion, the gradual build-up of inner rust layer contains a large amount of $\beta$-FeOOH with higher electrochemical activity. It is difficult for dissolved oxygen to transport at this time. In electrochemical tests, even small polarization can make $\beta$-FeOOH participate in cathodic reduction reaction, which leads to overestimating the electrochemical measurement result.

(4) Obtain the proportion of rust layers which participated in cathodic reduction reaction in deaerated condition, and further confirmed that the rust layers can be deoxygenized in the vicinity of corrosion potential.

(5) The current density of oxygen reduction reaction can be calculated by deducting the rust layers influence from corrosion current density. The results are coincided with mass loss, which illuminates that the corrosion current density after calibration can be really used to evaluate the corrosion rate.

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