Original article

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Study on the classification of seawater corrosivity of typical sea areas in China

https://doi.org/10.1515/corrrev-2020-0037
Received April 29, 2020; accepted May 4, 2020; published online July 27, 2020

Abstract: In order to evaluate the seawater corrosivity of typical sea areas in China and provide guidance for the seawater corrosion protection on marine equipment and facilities, field exposure test was carried out. These typical sea areas under various climatic zones in China included Qingdao, Zhoushan, Sanya and a South China Sea reef, and Q235, copper, 5083 aluminum alloy and 304 stainless steel were chosen as test materials. The continuous monitoring of seawater environmental factors (temperature, salinity, pH, dissolved oxygen, etc.,) and the statistical work of first-year corrosion rates of test materials were done. Then, based on the metal corrosion rates method and the environmental factors method, the seawater corrosivity of these typical sea areas in China were classified, respectively. Furthermore, the classification results from the two methods were compared and analyzed.

Keywords: classification of seawater corrosivity; environmental factors; grey relational analysis; seawater corrosion.

1 Introduction

The corrosivity of the natural environment is one of the earliest concerns in the field of corrosion protection (Maldonado and Veleva 2015; Mendoza and Corvo 1999; Rawat 1976; Singh 1986). The classification of the corrosivity of various types of environments in different areas can effectively guide the material selection and maintenance of facilities and equipment in a specific area. Among them, the evaluation and classification of atmospheric corrosivity have been studied systematically. Internationally, ISO 9223-1992 "Corrosion of Metals and Alloys – Corrosivety of Atmospheres – Classification" is widely used in this respect (Cui et al. 2013; Mikhailov et al. 2004; Veleva and Maldonado 1998). The standard was revised in 2012. Compared with the original version, a new category CX representing extremely high corrosivity was added. As a result, the corrosivity of the atmosphere is divided into six categories: C1(Very low), C2(Low), C3(Medium), C4(High), C5(Very high), and CX(Extreme) now (ISO/TC156 2012). The problem of soil corrosivity is more complicated, but the standards for corrosivity classification are already in the stage of use and adjustment. Internationally, the evaluation methods of West German standard DIN50929 and American ANSIA21.5 standard are relatively popular and universal (Ruppert et al. 2017; Yi et al. 2004).

However, regarding the classification of the seawater corrosivity, there is currently no uniform standard in the world, and it is still in the tentative exploration stage. Phull et al. (1997) once carried out seawater environmental tests for up to five years at typical seawater test sites in the world using 5086 aluminum alloy, B10 copper alloy and copper-containing carbon steels, and explained the effects of marine environmental factors on corrosion at different test sites. But, no further work was done. No standards and evaluation methods for classifying the seawater corrosivity was established. Zhu and Huang (2003) proposed an exploratory method to evaluate and classify the seawater corrosivity, based on the data of the main environmental factors in various sea areas in China, the local corrosion depth data of some carbon steels and low-alloy steels, and the grey relational analysis results. The seawater corrosivity was divided into five categories C1–C5 by the value of seawater temperature and fouling areas. However, this method was only suitable for carbon steel and low alloy steel materials, and its scalability was limited. In this work, through the continuous monitoring of seawater environmental factors (temperature, salinity, pH, dissolved oxygen, etc.,) and the statistical work of first-year corrosion rates of test materials at typical sea areas under various climatic zones in China, two kinds of evaluation methods

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were proposed. The seawater corrosivity of these typical sea areas was classified by means of metal corrosion rate method and environmental factors method, respectively, which provided a basis for the selection of materials and protective measures in seawater environments subject to the demands of the facilities, particularly with regard to service life.

2 Materials and methods

Q235 carbon steel, copper, 5083 aluminum alloy, and 304 stainless steel (chemical composition were shown in the Table 1) were chosen as the test materials, which were obtained from commercial sources. The specimen size was 200 × 100 × 4 mm, and the long edge of specimens was perpendicular to the rolling direction. The test sea areas were selected as Qingdao, Zhoushan, Sanya and a South China Sea reef (Abbreviated as SCS reef) away from mainland. Referring to "GB/T 6384-2008" (CSIC 2009), degreasing was done on the surface by washing with ethanol, and the specimen size (length and width measurement accuracy: 0.05 mm, thickness measurement accuracy: 0.02 mm) and weight M (Sartorius AG-LA1200S, accuracy: 0.001 g) were accurately measured and recorded before test. Then, all the specimens (three parallel specimens for each material) were fixed on the specimen frame and placed in the seawater at least 1 m below the lowest tide level. The specimens were perpendicular to the sea level. At the same time, a seawater environmental factor measurement device (SeaGuard RCM, which can monitor temperature, salinity, dissolved oxygen content, and pH of the sea water.) was put in place to in-situ monitor the seawater environmental factors data in each test sea area. After one year, specimens were retrieved and the environmental factors data were collected.

After removal of the corrosion products following the standard "ISO 8407-2009" (ISO/TC156 2009), the weight M_1 was recorded using Precision Balance. The corrosion rate R_{corr} (mm/y) was calculated according to formula(1), among which, M is the weight of the specimen before test (g); M_1 is the weight of the specimen after derusting (g); S is the total surface area of the specimen (cm^2); T is the test period (h); D is the material density (kg/m^3). Three parallel groups of test were repeated.

$$R_{\mathrm{corr}} = \frac{8.76 \text{ ñ } 10^7 \text{ ñ } (M - M_1)}{STD} \tag{1}$$

Based on the accumulated data, the seawater corrosivity of these typical sea areas in China were classified by applying the metal corrosion rates method and the environmental factors method, respectively.

3 Classification of seawater corrosivity by means of metal corrosion rates method

In order to classify the seawater corrosivity of typical sea areas in China, a comprehensive evaluation based on the corrosion data of test materials in these sea areas is required. Figure 1 and Figure 2 respectively show the morphologies and corrosion rates of Q235, copper, 5083 aluminum alloy, and 304 stainless steel exposed for one year at sea areas of Qingdao, Zhoushan, Sanya, and a SCS reef. These test sites cover China's main adjacent sea areas (Yellow Sea, East China Sea to South China Sea), and each is under a typical climatic zone, which can ensure the universality and rationality of the classification results.

Referring to the ISO 9223-2012 standard (ISO/TC156 2012), it is assumed that the logarithm of the seawater corrosion rate (ln(R_{corr}), set as x) in different sea areas meets the normal distribution. Based on the measured values of the first-year corrosion rates in Figure 1, a normal distribution function can be established for each test material according to the following formula (2) (Strutt et al. 1985).

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \tag{2}$$

In the formula, μ is the mean value of the normal distribution variable ln(R_{corr}), and σ is its standard deviation. On the horizontal axis, the area of a certain interval under the normal curve reflects the probability that the value of the variable falls in the interval, and it can be represented by P(x).

Define: $P(x \le \ln(R_{corr1}))$ or $P(x > \ln(R_{corr5})) = 10\%$

$P(\ln(R_{corr1}) < x \le \ln(R_{corr2}))$ or $P(\ln(R_{corr4}) < x \le \ln(R_{corr5})) = 15\%$

$P(\ln(R_{corr2}) < x \le \ln(R_{corr3}))$ or $P(\ln(R_{corr3}) < x \le \ln(R_{corr4})) = 25\%$

The values of R_{corr1}, R_{corr2}, R_{corr3}, R_{corr4}, and R_{corr5} can classify the seawater corrosivity into six categories. After

Table 1: Main chemical compositions of test materials (wt%).

	C	Si	Mn	Ni	Cr	Mo	S	P	Mg	Cu	Al	Fe
Q235 carbon steel	0.21	0.14	0.35	-	-	-	0.006	0.02	-	-	0.017	Rest
Copper	-	-	-	-	-	-	0.005	-	-	Rest	-	0.005
5083 aluminum alloy	-	0.14	0.72	-	0.07	-	-	-	4.3	0.086	Rest	0.138
304 stainless steel	0.049	0.38	1.49	8.09	18.08	0.056	0.003	0.022	-	0.14	-	Rest

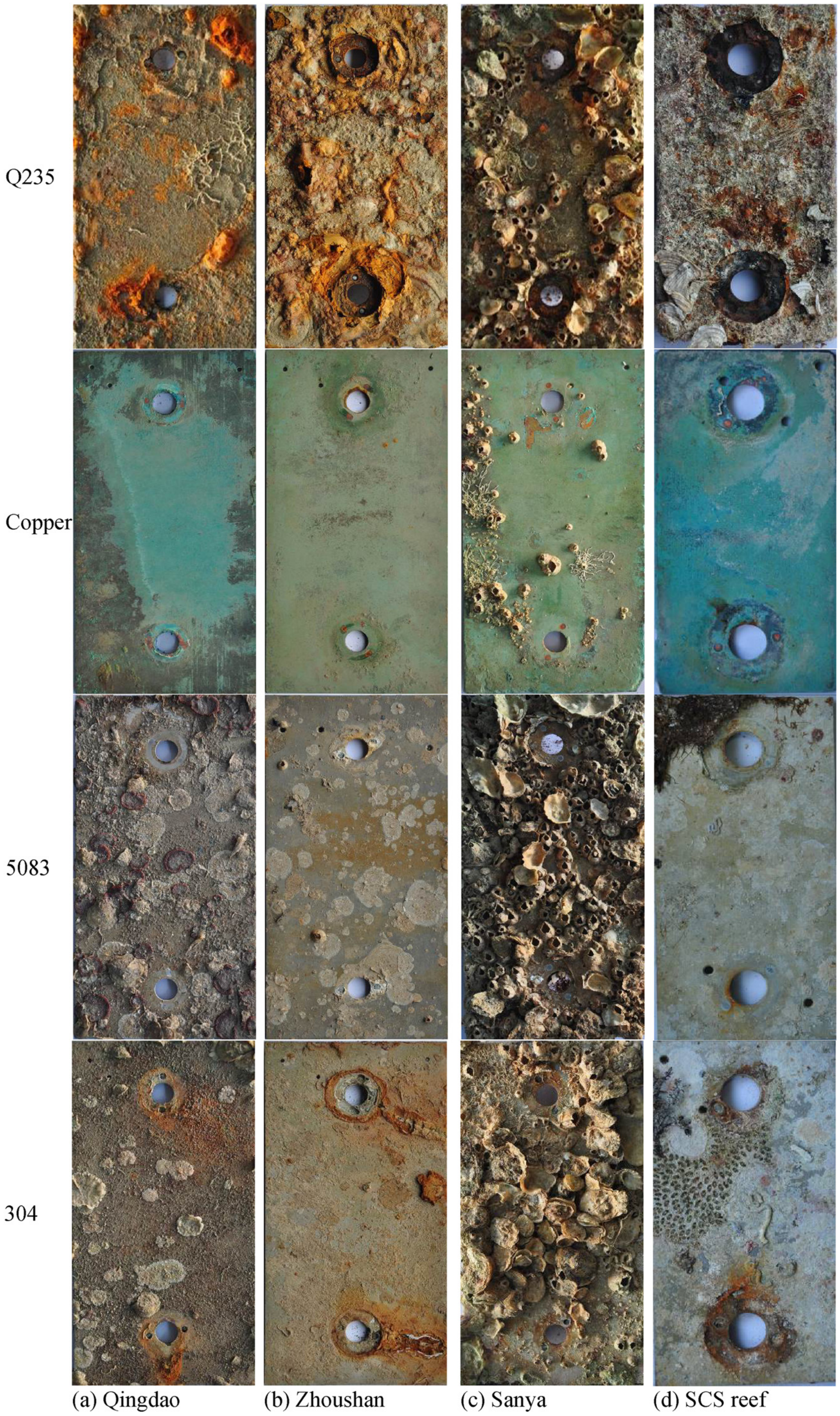

Figure 1: First-year corrosion morphologies of test materials in typical sea areas of China.

rounding the calculated values, the divided seawater corrosivity categories and corresponding corrosion rate ranges for each test metal are shown in Table 2.

The classification results of seawater corrosivity of typical sea areas in China are shown in Table 3. For carbon steel, the seawater corrosivity of the SCS reef is highest, reaching C5, while it is the lowest for Qingdao (C1). The seawater corrosivity of Sanya and Zhoushan are in between, but it is closer to C5 for Sanya. For copper, the rule is basically the same. Overall, the seawater corrosivity gradually increases from north to South (Qingdao to the SCS reef).

The seawater corrosivity classifications of different sea areas in China for aluminum are almost the same (except

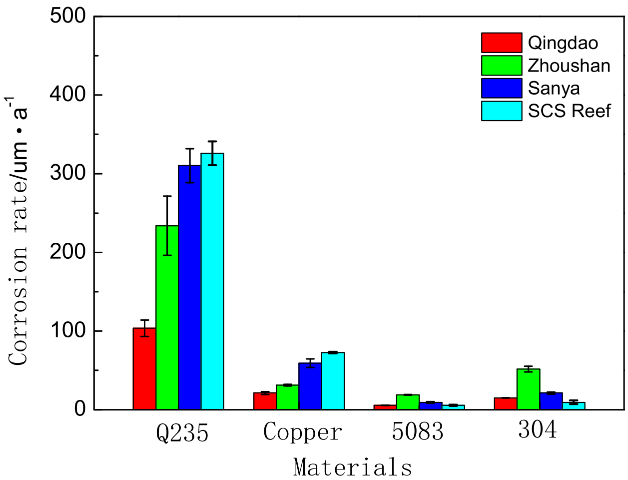

Figure 2: First-year corrosion rates of test materials in typical sea areas of China.

Qingdao) to that for stainless steel. In the sea area of Zhoushan, the seawater corrosivity is the highest, and both reach the category CX for aluminum and stainless steel. Followed by Sanya, it reaches C4. Different from carbon steel and copper, the seawater corrosivity of the SCS reef is the lowest (C2). For the corrosion-resistant metals such as aluminum and stainless steel, they rely on passivation film to obtain good corrosion resistance (Cui et al. 2019). However, in the sand-containing seawater environment of Zhoushan (The sand content of Zhoushan is 97.2 mg/L, while it is 23.2 mg/L, 15.0 mg/L, and 1.6 mg/L for Qingdao, Sanya and the SCS reef, respectively.), it can be speculated that the passivation film was constantly damaged due to the erosion of sediment, resulting in a high corrosion rate (Figure 3) (Yong et al. 2001; Liu et al. 2019). Thus, the seawater corrosivity of Zhoushan was extremely high. In the sea area of Sanya, as a large number of marine organisms such as oysters and barnacles attached and grew on the metal surface, local crevice corrosion occurred, and this could cause a large corrosion loss (Tian et al. 2018). So, the seawater corrosivity of Sanya was also relatively high.

Table 3: Seawater corrosivity categories of typical sea areas in China based on metal corrosion rates.

Test sites	Carbon steel	Copper	Aluminum	Stainless steel
Qingdao	C1	C2	C2	C3
Zhoushan	C4	C3	CX	CX
Sanya	C4	C4	C4	C4
SCS reef	C5	C5	C2	C2

Due to the low temperature, the corrosivity was relatively low for Qingdao. In contrast, in the sea area of the SCS reef, although it had a high temperature, most of the fouling organisms were algae, which were not prone to crevice corrosion. In addition, the content of calcium and magnesium ions in the sea water was relatively high, and the pH was slightly alkaline, which had a good protective effect on the passivation film. As a result, its seawater corrosivity was low.

Since obvious local corrosion occurred for aluminum alloy and stainless steel, using local corrosion depths for seawater corrosivity classification will be more accurate and meaningful. The data of local corrosion depths of 5083 aluminum alloy, and 304 stainless steel exposed for one year in different sea areas in China were shown in Table 4. The same method was applied for corrosivity classification (Table 5), and the results based on local corrosion depths (Table 6) were very close to that based on corrosion rates. This reflected the corrosion rates can indicate the severity of local corrosion to a certain extent (Forgeson et al. 1960), and further confirmed the reliability and rationality of the classification results based on the corrosion rates.

On the whole, the seawater corrosivity for metals with (non-uniform) general corrosion (such as carbon steel and copper) shows an increasing trend from north to South. For corrosion-resistant metals (such as aluminum and stainless steel), the seawater corrosivity is likely related to specific seawater environment like sand-containing

Table 2: First-year corrosion rates for different corrosivity categories.

Category	Corrosivity	Corrosion rates of metals R_{corr} (μm·a^{-1})			
		Carbon steel	Copper	Aluminum	Stainless steel
C1	Very low	$r \le 112$	$r \le 20$	$r \le 4$	$r \le 8$
C2	Low	$112 < r \le 155$	$20 < r \le 28$	$4 < r \le 6$	$8 < r \le 12$
C3	Medium	$155 < r \le 220$	$28 < r \le 41$	$6 < r \le 9$	$12 < r \le 20$
C4	High	$220 < r \le 320$	$41 < r \le 60$	$9 < r \le 13$	$20 < r \le 32$
C5	Very high	$320 < r \le 440$	$60 < r \le 85$	$13 < r \le 18$	$32 < r \le 50$
CX	Extreme	$r > 440$	$r > 85$	$r > 18$	$r > 50$

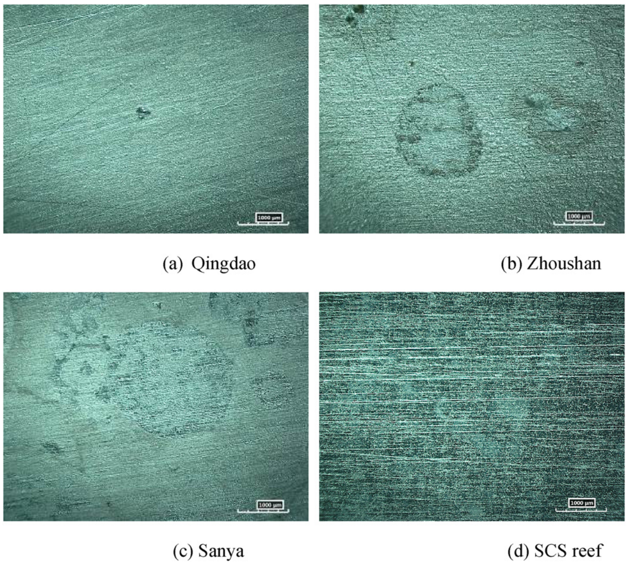

Figure 3: Micro-morphologies of 5083 aluminum alloy samples after removal of the corrosion products.

Table 4: First-year local corrosion depths of corrosion-resistant metals in typical sea areas of China.

Test sites	Local corrosion depths (mm)	
	5083 aluminum alloy	304 stainless steel
Qingdao	0.10	1.14
Zhoushan	0.45	2.23
Sanya	0.27	1.42
SCS Reef	0.07	0.62

seawater. Particularly, the seawater corrosivity classification results based on local corrosion depths are very close to that based on corrosion rates for these corrosion-resistant metals. The classification method based on corrosion rates is feasible.

Table 5: First-year local corrosion depths for different corrosivity categories.

Category	Corrosivity	Local corrosion depths (mm)	
		Aluminum	Stainless steel
C1	Very low	$d \leq 0.06$	$d \leq 0.60$
C2	Low	$0.06 < d \leq 0.10$	$0.60 < d \leq 0.85$
C3	Medium	$0.10 < d \leq 0.17$	$0.85 < d \leq 1.20$
C4	High	$0.17 < d \leq 0.30$	$1.20 < d \leq 1.75$
C5	Very high	$0.30 < d \leq 0.52$	$1.75 < d \leq 2.45$
CX	Extreme	$d > 0.52$	$d > 2.45$

Table 6: Seawater corrosivity categories of typical sea areas in China based on metal local corrosion depths.

Test sites	Aluminum	Stainless steel
Qingdao	C2	C3
Zhoushan	C5	C5
Sanya	C4	C4
SCS reef	C2	C2

4 Classification of seawater corrosivity by means of environmental factors method

The corrosion behaviors of metals are largely determined by the specific seawater environmental factors in different sea areas. These environmental factors include pH, salinity, temperature and dissolved oxygen, etc., (Selvara et al. 2004; Roychowdhury et al. 2004). Considering that it is difficult to quantify biofouling information such as types of fouling organisms, copper with little biofouling is selected as the research object. Grey relational analysis was applied to explore the correlation between environmental factors and copper corrosion rates. Based on these grey relational analysis results, the seawater corrosivity was evaluated and classified. Data of environmental factors (set as comparison series) and corrosion rates (set as reference series) of copper exposed for one year in typical sea areas in China were listed in Table 7. All the data were dealt with method of dimensionless processing, and then the grey relational degree (Table 8) of each environmental factor to the corrosion rates was calculated according to the following formula (3) (Mu et al. 2011; Ding et al. 2019).

$$\gamma_i = \frac{1}{4}\sum_{k=1}^{4}\frac{\underset{i}{Min}\ \underset{k}{Min}\Delta_i(k) + \rho \underset{i}{Max}\ \underset{k}{Max}\Delta_i(k)}{\Delta_i(k) + \rho \underset{i}{Max}\ \underset{k}{Max}\Delta_i(k)} \tag{3}$$

In the formula, k takes the value of 1–4, corresponding to different test sea areas; i respectively takes the value of 1–4, corresponding to four kinds of environmental factors (comparison series); $\boldsymbol{\Delta_i(k)}$ is the absolute difference of each data point between the comparison series i and the reference series in the same sea area; $\underset{i}{\mathrm{Min}}\ \underset{k}{\mathrm{Min}}\Delta_i(k)$ is the secondary minimum difference among $\boldsymbol{\Delta_i(k)}$ between all the comparison series and the reference series; $\underset{i}{\mathrm{Max}}\ \underset{k}{\mathrm{Max}}\Delta_i(k)$ is the secondary maximum difference among $\boldsymbol{\Delta_i(k)}$;

Table 7: Data of seawater environmental factors and corrosion rates of copper in different sea areas (after dimensionless processing).

Test sites	pH	Salinity (‰)	Temperature (°C)	Dissolved oxygen (mL/L)	Corrosion rate (μm/a)
Qingdao	0.986	1.012	0.659	1.047	0.460
Zhoushan	0.943	0.829	0.828	1.117	0.678
Sanya	1.004	1.051	1.217	0.804	1.286
SCS reef	1.067	1.108	1.297	1.032	1.577

Table 8: Grey relational degree γ of environmental factors to corrosion rates of copper.

Environmental factors	Corrosion rates of copper	
	γ	Order
pH	0.542	3
Salinity	0.601	2
Temperature	0.796	1
Dissolved oxygen	0.451	4

Parameter ρ is the resolution coefficient ($0 < \rho < 1$), whose value depends on the specific circumstance, and generally it takes the value of 0.5; γ_{0i} is grey relational degree of comparison series i, and it indicates a good correlation when its value is close to 1.

Then, the concept of seawater corrosivity evaluation factor Q is introduced (Zhu and Huang 2003; Zhu and Zhang 2000):

$$Q = \sum_{n=1}^{2} (Y_i \tilde{n} \gamma_i) \tag{4}$$

In the formula, Y_i is the value of two main environmental factors (after mean processing); γ_i is the corresponding grey relational degree. In this case, the two environmental factors which have greater influence on the corrosion rates of copper according to grey relational analysis results (Table 8) are temperature and salinity. The sum of their products (Q) is taken as the evaluation base of seawater corrosivity.

Table 9 shows the calculated values of seawater corrosivity evaluation factor Q of different sea areas. The larger Q, the higher the seawater corrosivity. For example, the Q value of the SCS reef is the largest, reflecting its highest seawater corrosivity, and meanwhile the corrosion rate of copper in the sea area of the SCS reef is also the largest. On the whole, the value of Q increases from Qingdao, Zhoushan to Sanya and the SCS reef, which is basically consistent with the law of copper corrosion rates in different sea areas.

Based on the mean value μ and standard deviation σ ($\mu-\sigma$, $\mu-0.5\sigma$, μ, $\mu + 0.5\sigma$, $\mu + \sigma$, respectively) of Q, the seawater corrosivity can be divided into six categories.

Table 9: Seawater corrosivity evaluation factors Q of typical sea areas.

Test sites	Q
Qingdao	1.132
Zhoushan	1.157
Sanya	1.600
SCS reef	1.698

Table 10 gives the value ranges of Q corresponding to each seawater corrosivity category.

Referring to Table 9 and Table 10, the seawater corrosivity of typical sea areas in China was classified, as shown in Table 11. Compared with the classification results by means of metal corrosion rates method (Table 3), the categories were the same for Qingdao and the SCS reef, while they were close with a deviation of no more than one level for Zhoushan and Sanya. This reflected the relative rationality and reliability of the seawater corrosivity classification method.

The above two methods are an attempt to classify the seawater corrosivity. The methods can be for reference, but more efforts are needed. At present, limited by reasons such as the small number of test sites, insufficient coverage, and inadequate monitoring of seawater environmental factors (especially other key environmental factors that may affect the corrosion rates), the classification is not fine enough, and there are some deviations and uncertainties to a certain degree. Based on more subsequent seawater environmental tests and comprehensive

Table 10: Value ranges of Q for different corrosivity categories.

Category	Corrosivity	Q
C1	Very low	$Q \leq 1.10$
C2	Low	$1.10 < Q \leq 1.25$
C3	Medium	$1.25 < Q \leq 1.40$
C4	High	$1.40 < Q \leq 1.55$
C5	Very high	$1.55 < Q \leq 1.70$
CX	Extreme	$Q > 1.70$

Table 11: Seawater corrosivity categories of typical sea areas in China by means of seawater environmental factors method.

Test sites	Categories
Qingdao	C2
Zhoushan	C2
Sanya	C5
SCS reef	C5

accumulation of seawater environmental factors (including marine organisms), the seawater corrosivity classification methods can be further improved to make the classification results more precise and reliable, which is also a focus of our follow-up work.

5 Conclusions

(1) A method of seawater corrosivity classification based on the corrosion rates of metals was established. For carbon steel and copper, from Qingdao, Zhoushan, Sanya to the SCS reef (from North to South regionally), the seawater corrosivity increases on the whole.
(2) The seawater corrosivity classifications of different sea areas in China for aluminum are almost the same (except Qingdao) to that for stainless steel. The seawater corrosivity is the highest (CX) for Zhoushan, followed by Sanya, and it is the lowest for the SCS reef (C2). For these corrosion-resistant metals, the seawater corrosivity classification results based on local corrosion depths are very close to that based on corrosion rates.
(3) A method of seawater corrosivity classification based on environmental factors was established. Compared with the classification results by means of metal corrosion rates method, the deviation of seawater corrosivity classification of each sea area is less than one level, which reflects the relative rationality and reliability of the classification method. In the follow-up work, carrying out more seawater environment tests and comprehensively accumulating seawater environmental factors are needed.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: This work was finically supported by the National Natural Science Foundation of China (No. 51931008).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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