Modeling of the Critical Pitting Temperature between the Laboratory-Scale Specimen and the Large-Scale Specimen

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Critical pitting temperature (CPT) of 316L stainless steel with different specimen areas in 3.5 wt% NaCl solution was investigated by the potentiostatic method. The results showed that the CPT exhibited a decreasing tendency with the increase in specimen areas, which was attributed to the higher probability for large-scale specimens to attain a large pit depth than small specimens. Therefore, stable pitting is easier to form, resulting in a lower CPT. Subsequently, a Gumbel extreme function was applied to establish a model correlating CPT with the specimen area. The CPT was linear with the double logarithm of the specimen area and could be accurately predicted for large-scale specimens.

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Stainless steel has been commonly used in different corrosive environments, such as acid corrosion, marine corrosion, and industrial corrosion, due to its excellent corrosion resistance.1–9 However, it can always experience pitting corrosion during the service period,3–18 resulting in material failure by penetration and enormous safety problems. In addition to the aggressive corrosion environment, the temperature is another important factor that affects the pitting behavior of stainless steels. According to Brigham and Tozer,1 there is a critical pitting temperature (CPT), which is the lowest temperature at which the growth of stable pits is possible. In other words, materials are free of pitting failure when the temperature is lower than CPT. Therefore, the measurement of CPT is of significance in practical engineering.

A large number of methods, such as traditional immersion method, polarization curve (PC) method, and electrochemical noise (EN) technology,12–17 can be used to measure the CPT in laboratory research. Meanwhile, based on the traditional technology, the improvement in EN and the application of the electrochemical impedance spectrum (EIS) further upgrade the measurement technology of CPT.18,19 Nevertheless, all the above methods are limited to the laboratory scale. There is also no possibility of obtaining CPT for a large-scale specimen in practical engineering. Hence, it is necessary to develop a relationship for CPT between laboratory-scale specimens and large-scale specimens since it is impractical to measure the CPT by using the electrochemical method and the time-consuming immersion method on engineering-scale structures. By generating a model, the CPT measured in the laboratory can be explored to predict the CPT of large-scale specimens, such as long pipelines, which is of great significance in engineering design.

In this study, first, we measured the CPT of a large number of specimens with different areas. Then, using the statistical stochastic theory, a predictive model of the CPT was established between small-area specimens and large-area specimens by using the Gumbel-I extreme distribution. Finally, the model was verified by large specimens, which is found to be consistent with the experimental data.

Experimental

Materials.—In this study, a commercial standard 316L stainless steel was used, with the following chemical composition (wt%): C: 0.018; Si: 0.49; Mn: 1.10; S: 0.001; Cr: 17.13; Mo: 2.15; Ni: 12.7; P: 0.036; and Fe balance.

The 316L stainless steel was cut into test samples of the following dimensions: 1 × 1 × 10 mm, 4 × 2.5 × 10 mm, 10 × 10 × 10 mm, 40 × 25 × 10 mm, and 50 × 100 × 10 mm. In order to avoid the crevice corrosion, the specimens were coated with epoxy powder coating first, whose adhesion force was more than 80 MPa,18,20 and then embedded in the epoxy resin leaving an exposed area of 0.01, 0.1, 1, 10, or 50 cm², respectively, as working electrode surfaces. The other end of the specimens was connected to a copper wire to create an electrical connection.

Before all experiments were carried out, the specimens were wet ground to a 1000 grit-finish by the abrasive paper, degreased with acetone, rinsed with deionized water, and dried in a compressed hot air flow. The test solution was 3.5 wt% NaCl solution, which was prepared with analytical grade reagents and deionized water.

CPT measurements.—A Zahner Zennium electrochemical workstation was used to carry out the electrochemical measurements. A standard three-electrode cell was used, where a platinum plate was applied as the counter electrode, a saturated calomel electrode (SCE) was as the reference electrode, and a 316L specimen was applied as the working electrode.

The measurements of the CPT were carried out by the potentiostatic method. Before the tests of CPT, the solution was deaerated with flowing nitrogen gas for 1 h. Then, several other steps were carried out. First, in order to eliminate oxides on the specimen surface for higher reproduction of the experiment, a potential of −900 mV vs SHE was applied on the specimen at an initial temperature of 1°C for 5 min.20 Subsequently, the specimen was stabilized at the open circuit potential (OCP) for 30 min to reach a steady state. Thereafter, an anodic potential of 942 mV vs SHE (700 mV vs SCE) was applied, and simultaneously, the temperature of the test solution was increased at a rate of 1°C·min⁻¹,12 which was regulated through a program-controlled water bath. The current was recorded by the electrochemical workstation at a frequency of 1 Hz with the increase in temperature. The experiment was stopped when the current density reached a value of 1 mA cm⁻². The CPT corresponds to the temperature when the current density exceeds 100 μA cm⁻² for 60 s.12 After each test, the surroundings of the specimens were checked through an optical microscope. If there was crevice corrosion between the specimen and the epoxy powder coating, the test result was discarded to ensure the quality of the measurement result.

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Results and Discussion

**CPT measurement results.**—As shown in Fig. 1, the CPT values of specimens with five different areas were measured by the potentiodynamic method. Fig. 1 indicates that the values of CPT for large-area specimens were lower than those for small specimens. In order to elucidate the effect of the specimen area on the CPT accurately, more than ten sets of experiments were carried out and a statistical method was also used to describe the distribution rules of CPT. The cumulative probability is defined as follows:

\[ F(t) = \frac{n}{N + 1} \]  

where \( t \) represents the CPT obtained from experimental results, \( n \) denotes the order corresponding to \( t \) for all CPT results by ranking the CPT values from small to large, and \( N \) denotes the total number of the experiments. Therefore, \( F(t) \) can be defined as the probability of CPT smaller than \( t \).

As shown in Fig. 2, the cumulative probabilities of CPT varied with areas for 0.01 cm\(^2\), 0.1 cm\(^2\), 1 cm\(^2\), 10 cm\(^2\) and 50 cm\(^2\) specimens. Fig. 2 showed that the average values of CPT for large specimens were smaller than those for small specimens. Moreover, the distribution of CPT was narrow for large-area specimens, which was within 2 °C, whereas, it was found to be dispersed for small-area specimens with a CPT distribution from 12 °C to 23 °C. The results were found to be consistent with those of Peguet,\(^{21}\) who measured the CPT of the 2205 duplex stainless steel by using a potentiodynamic method and demonstrated a broad distribution of CPT for small-area specimens and the extreme distribution of CPT within 1 °C when the area approached to infinity.

The phenomenon that larger specimens have a lower CPT can be explained by the theory of stable pitting. As CPT is the lowest temperature for the formation of a stable pit, any factor that is beneficial for stable pitting growth will lead to a low CPT. Generally, the pitting process is considered involve pit nucleation and pit growth,\(^{22,23}\) which are affected by several factors, such as the size and the composition of inclusions, the microstructure of the material, and the component and the structure of pitting lacy covers, etc. Pit nucleation mainly originates from the heterogeneous locations of the component and the microstructure on the metal surface, particularly the sites of nonmetallic inclusions.\(^{24–34}\) Once a pit nucleates, the metal in the pit dissolves and grows. Whether a pit nucleus can survive to a stable pit is dependent on the inner chemistry of a pit, which is a competition between the dissolution of metals in a pit and the diffusion of ion out of a pit. Therefore, it is easier to maintain an aggressive pit chemistry for the metal with a larger dissolution rate and a deeper pit (lower diffusion rate). According to the theory of the pit stability product,\(^{23,35,36}\) a pit can grow stably without repassivation when the chemistry in a pit is aggressive enough to maintain an undercutting pit growth.\(^{34,36–38}\) As smaller inclusions are easier to passivate than larger inclusions after dissolution, the dissolution of larger inclusions is easier to grow into a deeper pit, thus promoting the formation of stable pits. Meanwhile, the pitting growth kinetics are affected by several factors, especially the pitting lacy cover.\(^{20,27,38,39}\) Under the effect of the osmotic pressure caused by the differential concentration between the pit solution and the bulk solution, the lacy cover collapses easily. As a result, the pit solution at high concentration diffuses out of the pit and the aggressive inner chemistry is diluted by the bulk solution. Consequently, repassivation occurs.\(^{10,36,39}\) On the contrary, if the lacy cover is firm enough, it will retain the corrosive inner chemistry as a barrier.\(^{36–38}\) Under the effects of acidification and autocatalysis, the metal in the pit dissolves much faster. As a result, the metastable pit grows into a stable one. The components and the microstructures of the nonmetallic inclusions are primarily affected by the metallurgical factors, whereas, the properties of the pitting lacy covers are the interactive effect between the material itself and the corrosion environment. For large-scale specimens, on the one hand, the number of nonmetallic inclusions is larger than that in small specimens as they contain larger surface areas, which increases the probability of pit nucleation and the stable pit growth as well. On the other hand, as the distribution of inclusions is stochastic, from the perspective of probability statistics, there is a high opportunity or probability for large-scale specimens to contain large inclusions and firm lacy covers than small specimens. Therefore, for large-scale specimens, it is easier to grow into a stable pitting and, as a result, to obtain a lower CPT.

Taking into consideration the CPT theory provided by Newman previously, there is a critical current density for passivation, \( i_{\text{crit}} \), depending on the maximum dissolution rate of the metal, which increases with the temperature.\(^{37,40}\) There is also a limiting diffusion current density, \( i_{\text{lim}} \), which is obtained from the saturation concentration of the pit chemistry and increases more gradually with temperature than \( i_{\text{crit}} \).\(^{34,37,40}\) The CPT corresponds to the temperature where \( i_{\text{crit}} = i_{\text{lim}} \), because below this temperature the metal cannot dissolve at a sufficient rate required to precipitate the salt film.\(^{34,37,48}\)

According to the first law of Fick,\(^{40}\)

\[ i_{\text{lim}} = \frac{zFDC_{\text{sat}}}{\delta} \]  

where \( z \) represents the number of charge transfers, \( F \) is the Faraday constant, \( D \) denotes the diffusion coefficient, \( C_{\text{sat}} \) is the saturation solubility of the pit chemistry, and \( \delta \) represents the diffusion length. A deeper pit implies a larger diffusion length \( \delta \) and a smaller effective diffusion of the metal ion out of the pit, that is, a lower \( i_{\text{lim}} \). Consequently, the intersection of \( i_{\text{crit}} \) and \( i_{\text{lim}} \) gives rise to a lower temperature and hence the CPT decreases. With regards to large area specimens, there is a greater probability to obtain a large pit depth (large \( \delta \)). A large pit results in a less effective diffusion of the metal ion out of the pit.
pit (small \(i_{\text{lim}}\)), which will be beneficial for retaining an aggressive pit chemistry and creating a stable pitting. As CPT is the temperature at which pits can become stable, a lower CPT occurs for a deeper pit.

Salinas-Bravo and Newman previously concluded that the temperature range of CPT was correlated to the size distribution of pitting nucleation sites.\(^{15}\) In order to have a better understanding of the temperature ranges of CPT at different specimen areas, Fig. 3 below presents a straightforward illustration. \(i_{\text{lim}}\) represents the maximum dissolution current density of a material and reflects the corrosion resistance of the material itself. The value of \(i_{\text{lim}}\) is the interaction between the material and the corrosion environment, and has nothing to do with specimen areas. Therefore, we ignore the variation of \(i_{\text{crit}}\) in Fig. 3. The differential of CPT at different specimen areas is determined by the value of \(i_{\text{lim}}\). As the first law of Fick manifests, \(i_{\text{lim}}\) is inversely proportional to the diffusion length \(\delta\). Therefore, CPT is related to the largest pit depth formed on the material surface. For small area specimens, because of the inhomogeneity of the component and the microstructure of the material, the largest pit depth which might formed on the material surface varies a lot from one specimen to another, resulting in a wider range of \(i_{\text{lim}}\). Hence, there is a wide range of CPT. In terms of the large-area specimens, the differences of the largest pit depth formed between specimens are small, leading to a similar \(i_{\text{lim}}\) and a narrow range of CPT.

The above analysis draws a conclusion that the CPT has a tendency to become lower for large-scale specimens than small-scale specimens. Meanwhile, Engelhardt and Macdonald have demonstrated that the pit depth deepens for large size specimens.\(^{31}\) Moreover, Burstein and Llevbare reported that the pitting potential decreased with the increase in the specimen area as well.\(^{42}\) In other words, the pitting event becomes more susceptible for the large-scale specimens than the small specimens on the laboratory scale. It is risky to evaluate the CPT of materials with large surface areas in practical engineering by the results of small area specimens in the laboratory. However, it is unrealistic to carry out measurements on large-scale samples. Therefore, it is necessary to establish a CPT model that can correlate the behavior of large-scale specimens with laboratory small-scale specimens for the prediction of CPT in practical engineering.

Establishment of the model of CPT for large-scale specimens.—

Establishment of the model.—The pitting events randomly occur on the surface of passive materials and the distribution of the largest pit depth follows the rules of statistics. The Gumbel-I extreme distribution function was first employed by Macdonald to predict the probability of pitting penetration and the largest pit depth in long-distance pipelines by extrapolating the experimental data in the laboratory to practical engineering.\(^{41}\) According to the first law of Fick (Eq. 2) and the CPT theory provided by Newman (that is, CPT corresponds to the interaction of \(i_{\text{crit}}\) and \(i_{\text{lim}}\)), it can be inferred that:

\[
\text{CPT} \propto i_{\text{lim}} \propto \frac{1}{\delta} \tag{3}
\]

Therefore, the largest pit depth corresponds to the smallest CPT. Now it is reasonable to infer that the distribution of CPT at different specimen areas may also conform to the Gumbel extreme distributions similar to the largest pit depth that follows the rule of Gumbel function. Moreover, Hinds et al. also used the Gumbel function to estimate the pitting potential for different area specimens.\(^{33}\) The pitting potential follows the extreme distribution well by proper conversion of the Gumbel function. Since the pitting potential has a negative correlation with the pit depth, the same as for CPT, it is suitable to describe the variation of CPT with specimen areas by the Gumbel extreme function.

Based on the Gumbel function of the largest pit depth,\(^{42}\) the Gumbel function of CPT can be expressed as follows:

\[
F(t) = \exp[-\exp(y')]
\]

\[
y' = \ln[\ln(\frac{1}{F(t)})] = \frac{t - \mu'}{\alpha'} \tag{4}
\]

where \(t\) represents the measured CPT in the experiment, \(\mu'\) and \(\alpha'\) are the modified location parameter and scale parameter of the pit, respectively, \(F(t)\) is the cumulative probability (see Eq. 1), and \(y'\) is the reduced variate of \(F(t)\). Therefore, the linear function between the reduced variate of the cumulative probability \(y'(t)\) and CPT \(t\) for a certain specimen area, \(s\), can be described as:\(^{43}\)

\[
y' = \ln[\ln(\frac{1}{F(t)})] = \frac{t - \mu'}{\alpha'} \tag{5}
\]

In order to present the effect of specimen area on CPT, a size parameter \(R\), which represents the ratio of the large area (\(S\)) to the small area (\(s\)), must be introduced into Eq. 6. Referring to the Gumbel function of the maximum pit depth (recorded as \(X_{\text{max}}\) for simplification), it can be assumed that there are \(N\) sets of experiments and \(n\) represents the \(n^{th}\) experiment (\(n\) varies from 1 to \(N\)). When ranking the \(X_{\text{max}}\) values of \(N\) sets of experiments from small to large, i.e., \(X_{\text{max},1}, X_{\text{max},2}, \ldots, X_{\text{max},n-1}, X_{\text{max},n}\), the \(X_{\text{max},n}\) represents the \(X_{\text{max}}\) of \(N\) sets of experiments and \(X_{\text{max},n}\) reflects the \(X_{\text{max}}\) of \(n\) sets of specimens respectively. Therefore, the ratio of specimen areas is represented by the ratio of the ordinal number, that is,

\[
R = \frac{S}{s} = \frac{N}{n} \tag{6}
\]

By Eq. 7, the size parameter \(R\), can be introduced into Eq. 6 to develop a relation between different specimen areas for the estimation of CPT, as Eq. 8 shows below:

\[
\frac{1}{F(t)} = \frac{N + 1}{n} = \frac{N + 1}{N} \cdot R \tag{7}
\]

Therefore, the CPT of the large-scale specimen with an area of \(S\) can be derived as follows:

\[
\text{CPT} = \mu' + \alpha' \ln \left[ \ln \left( \frac{N + 1}{N} \cdot \frac{S}{s} \right) \right] \tag{8}
\]

Eq. 9 describes the variation of CPT with specimen areas and establishes the relationship of CPT between large-scale specimens and small-scale specimens, where \(\mu'\) and \(\alpha'\) are obtained from the small-area specimen in the laboratory, and \(S/s\) reflects the amplification ratio of large-scale specimen versus the small one. However, there is still one more question that needs to be considered, that is, what extent do the experimental sets, \(N\), affect the accuracy of the model. The value \(N=1\) becomes equivalent to \(N\) when the set of experiments \(N\) approaches to infinity. Then, the amplification ratio \(R\) becomes equal to the reciprocal of the cumulative probability (see Eq. 8). Therefore, the deviation can be expressed as follows:

\[
d = t_N - t_\infty = \frac{\alpha' \ln[\ln(N + 1)R/N] - \alpha' \ln[\ln R]}{\mu' + \alpha' \ln[\ln R]} \tag{9}
\]
Consequently, a reasonable small amplification ratio, $R$, the theoretical prediction value of CPT ($\alpha$ area of 1cm$^2$ were used as an example to establish the CPT model cases of small amplification ratios. were calculated from $R$ bigger one, $R = 10000$, were taken as examples, and the deviations were calculated from $N$ equals one to twenty separately, as displayed in Fig. 4. It can be seen in Fig. 4 that the deviations converge to zero. That is, the bigger the amplification ratio $R$, the more the experimental sets $N$, and hence the smaller the deviations. For large-scale specimens in practical engineering, it is unnecessary to consider the effect of experimental sets on prediction accuracy because the amplification ratio is large. For the sake of reliability, more than five sets of experiments are recommended for the linear fitting precision of $\mu'$ and $\alpha'$ and for cases of small amplification ratios.

In this study, 15 sets of CPT of relative small-area specimens with an area of 1cm$^2$ were used as an example to establish the CPT model

$$d < \frac{\ln\left(\frac{N+1}{R}\right)}{\ln\left(R\right)} - 1 \quad \text{[11]}$$

where $t_N$ is the CPT estimated by $N$ sets of experiments, and $t_L$ is the theoretical prediction value of CPT ($N$ approaches to infinity). Consequently, a reasonable small amplification ratio, $R = 10$, and a bigger one, $R = 10000$, were taken as examples, and the deviations were calculated from $N$ equals one to twenty separately, as displayed in Fig. 4. It can be seen in Fig. 4 that the deviations converge to zero. That is, the bigger the amplification ratio $R$, the more the experimental sets $N$, and hence the smaller the deviations. For large-scale specimens in practical engineering, it is unnecessary to consider the effect of experimental sets on prediction accuracy because the amplification ratio is large. For the sake of reliability, more than five sets of experiments are recommended for the linear fitting precision of $\mu'$ and $\alpha'$ and for cases of small amplification ratios.

In this study, 15 sets of CPT of relative small-area specimens with an area of 1cm$^2$ were used as an example to establish the CPT model

$$\text{Table I. Gumbel extreme analysis of the CPT based on 1 cm}^2\text{ specimen.}$$

| $n$ | CPT (°C) | $F(t)$ | $\ln\left[\ln\left(1/F(t)\right)\right]$ |
|-----|----------|--------|----------------------------------|
| 1   | 10.6     | 0.0435 | 1.14263 |
| 2   | 12.8     | 0.087 | 0.88975 |
| 3   | 12.9     | 0.1304 | 0.71155 |
| 4   | 13.3     | 0.1739 | 0.5592 |
| 5   | 13.5     | 0.2174 | 0.42266 |
| 6   | 13.8     | 0.2609 | 0.29537 |
| 7   | 13.9     | 0.3043 | 0.17374 |
| 8   | 14       | 0.3478 | 0.05461 |
| 9   | 14.8     | 0.3913 | -0.06371 |
| 10  | 15       | 0.4348 | -0.18288 |
| 11  | 15.6     | 0.4783 | -0.30447 |
| 12  | 15.8     | 0.5217 | -0.42976 |
| 13  | 16.1     | 0.5652 | -0.56111 |
| 14  | 16.3     | 0.6087 | -0.70031 |
| 15  | 16.6     | 0.6522 | -0.85003 |
| 16  | 16.9     | 0.6957 | -1.0138 |
| 17  | 17       | 0.7391 | -1.19626 |
| 18  | 17.1     | 0.7826 | -1.40595 |
| 19  | 17.8     | 0.8261 | -1.65528 |
| 20  | 18       | 0.8696 | -1.9681 |
| 21  | 18.5     | 0.913 | -2.39668 |
| 22  | 19       | 0.9565 | -3.11284 |

Figure 4. Deviations of the CPT derived from limited experimental sets. (Contrast to the sets of experiments $N$ approach to infinity).

for the prediction of CPT with large areas. The CPT results in the laboratory are displayed in Table I as well as the cumulative probability ($F(t)$) and the reduced variate ($\mu'$) according to Eqs. 1 and 6. A good linear relationship between the reduced variate and CPT is presented in Fig. 5, which indicates that the variation of CPT for large-scale specimens follows the extreme distribution, and the Gumbel extreme function was considered to be suitable for the prediction of CPT. As shown in Table II, the location parameter $\mu'$ and the scale parameter $\alpha'$ of the pit could be calculated easily based on Fig. 5 and Eq. 6. Therefore, the CPT of the large-scale specimens could be described as follows:

$$CPT_t = 14.43 - 2.04\ln\left[\ln\left(16S/15x_t\right)\right] \quad \text{[12]}$$

Eq. 12 is the theoretically calculated formula of CPT for 316L stainless steel in 3.5% NaCl solution obtained from 1cm$^2$ specimens, which manifests that the CPT of large-scale specimen is linear with the double logarithm of the specimen area. According to Eq. 11, the deviation of 15 sets of experiments at an amplification ratio of 10 is less than 3.3%, which is a relatively small and acceptable value, as seen in Fig. 4. Therefore, the results of CPT of large-area specimens in practice can be successfully obtained by extrapolating from the laboratory results.

**Verification of the model.**—The above model in Eq. 12 shows an example derived from the 1cm$^2$ samples. It is required to be verified that whether the CPT model can be used for the prediction of large-scale specimens. The verification comes down to two aspects. One is the accuracy verification, that is, if the above model (Eq. 12) is accurate in predicting the CPT value for large-scale specimens. The other is the universality verification, that is, whether the predicted CPT values of large-scale specimens derived from different small-area specimens are identical.

Consequently, the accuracy verification was first carried out by using experimental data. As displayed in Fig. 1, the values of CPT of the 10 cm$^2$ specimens and the 50 cm$^2$ specimens were measured. Comparison between the experimental data and the predicted data of CPT is shown in Fig. 6, where the experimental data were taken as the average value of more than 10 sets of experiments. It can be concluded from Fig. 6 that the variation tendency of the predicted CPT is coincident with the experimental data. CPT decreases in the
first stage and then varies a small amount and approaches an ultimate value when the specimen area tends to become infinite. On the one hand, the opportunities or probabilities for the formation of a larger pit depth for large-area specimens tend to be bigger than that for small-area specimens (as the pit depth is random and dependent on the metallurgical factors), which is beneficial for the formation of a stable pitting, resulting in the decrease of the CPT. On the other hand, for large-scale specimens in practical engineering, the largest pit depth which may formed on the material surface is almost identical for different specimens as the component and the microstructure tend to be similar for the same metallurgical technology. Therefore, the CPT varies little as the specimen area extends to infinity. For example, consider a pipeline with a length of 2 m and a diameter of 10 cm, the ultimate value of CPT by the prediction model (Eq. 12) is 10.06, which is almost the same as the lowest measured value of CPT in the experiment (i.e., 10.2 for the 50 cm² specimen, see error bar in Fig. 6). In other words, the prediction model (Eq. 12) based on the Gumbel extreme distribution function can accurately predict the CPT of large-scale specimens.

Subsequently, the universality verification was implemented through verifying the consistency of the CPT of large-scale specimens obtained from different areas of small specimens. According to the above-mentioned method for the 1 cm² specimens, Table III displays the parameters of 0.01 cm² and 0.1 cm² specimens, and the prediction models are calculated. For the sake of easy comparison, the parameters of the 1 cm² specimen are also listed in Table III. The variation of μ and α’ improve gradually with the decrease in the specimen area (increase in the amplification ratio). Fig. 6 also shows the comparison of the predicted values of CPT derived from different small-area specimens. There is only a small difference among the three models, and the predicted CPT values can still be considered as identical by different prediction models, which manifests the universality of the CPT model.

Above all, the prediction model of CPT derived from the Gumbel extreme function provides a reliable prediction for the large-scale specimens, and the ultimate value of the CPT can be considered as a valid design reference in practical engineering. The results of this study also explain the discrepancy between the results of laboratory simulation and practical engineering. The severe corrosion problem in practice is not only related to the complexity of the service environment, but also connected to the specimen area. Moreover, the application of the extreme analysis in corrosion research was also expanded. The extreme distribution function cannot only be used in the analysis of the pit depth, but also in CPT research.

### Conclusions

The CPT values of 316L stainless steel with different specimen areas were tested by the potentiostatic method. The results showed that the CPT decreased with the increase in specimen areas. The distribution of CPT was narrow for large-area specimens, which was within 2°C, whereas, it was dispersed for small-area specimens with a CPT distribution from 12°C to 23°C. The temperature range of the CPT was related to the largest pit depth formed in each specimen.

A predictive model of CPT varying with specimen areas was established on the basis of the Gumbel extreme function. The variation tendency of the predicted CPT was found to be coincident with experimental data, indicating that CPT followed the Gumbel distribution and the model was able to predict the CPT of large-scale specimens accurately. CPT was found to be linear with the double logarithm of specimen area. As the areas approached infinity, CPT extended to an ultimate value, which could be considered as a theoretical prediction value to provide a valid design reference in practical engineering. The application of extreme analysis in corrosion research was also expanded, which cannot only be used in the analysis of the pit depth, but also in CPT research.

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**Table III. Scale and location parameters and the predicted models of the CPT under different specimen areas.**

| Specimen area | Scale parameter α′ | Location parameter μ’ | Predicted model |
|---------------|-------------------|----------------------|-----------------|
| 0.01 cm²      | −2.94             | 17.70                | \( CPT_{101} = 17.70 - 2.94 \ln[\ln(16S_{5.0})] \) |
| 0.1 cm²       | −2.32             | 15.57                | \( CPT_{1} = 15.57 - 2.32 \ln[\ln(16S_{5.0})] \) |
| 1 cm²         | −2.04             | 14.43                | \( CPT = 14.43 - 2.04 \ln[\ln(16S_{5.1})] \) |
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