International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

# Short Communication Corrosion of Q345B Steel in Soil Solution Extract Containing Chloride Ions

*Qian Wang, Linchun Zhang*<sup>\*</sup>, *Ailian Zhang* 

School of Civil Engineering, Sichuan College of Architectural Technology, Deyang 618000, China; \*E-mail:<u>zhanglinchun1980@126.com</u>

Received: 24 October 2021 / Accepted: 19 November 2021 / Published: 5 January 2022

As a common steel structure material, Q345B steel is widely used in outdoor steel structures, but there are few studies on the corrosion of the buried part of Q345B steel in the service process of potential chlorine ion pollution environments. Therefore, the corrosion behavior of Q345B steel in a soil solution contaminated by sodium chloride was investigated by using the open circuit potential, electrochemical impedance spectroscopy, potentiodynamic polarization, energy dispersion spectroscopy, laser scanning confocal microscopy and weight loss method. The results show that the corrosion product films formed by Q345B steel in different soil solutions are mainly composed of Fe oxide, and the material surface shows the coexistence of overall corrosion and local slight uneven corrosion. In soil contaminated by NaCl, the competitive adsorption of Cl<sup>-</sup> on the electrode surface of Q345B steel will reduce the self-corrosion potential of Q345B steel and improve the corrosion current. The solution resistance and charge transfer resistance of the soil leaching solution decreased, the weight loss rate of the materials increased, the number of corrosion active points increased, and the corrosion of Q345B steel was induced from light-colored and pitted corrosion to dark and banded corrosion. However, Cl<sup>-</sup> had no obvious effect on the formation and development of pitting corrosion of Q345B steel.

Keywords: Q345B, steel structure, chlorine, pollution

# **1. INTRODUCTION**

As a construction method with the largest amount of steel used in the construction industry, steel structures have a series of advantages of high strength, light dead weight, good seismic performance, good energy saving effect, and high degree of industrialization and have a broad application space[1-4]. However, outdoor steel structures have problems such as high height, long service cycle and difficult maintenance. Ordinary building steel easily rusts in air or humid environments, especially in environments containing acid, alkali and salt corrosion[5,6].

After the heavy snow in the winter, calcium chloride, sodium chloride and snowmelt agent tend

to be used to removesnow. Although they effectively achieve the purpose, withrain erosion, chloride flows and spreads everywhere, causing great pollution to plants, soil, buried parts of outdoor steel structures, which increases the potential of corrosion risk[7]. This corrosion affects the buried part of the steel structure, causes stress concentration and accelerates the advance failure of the steel structure[8]. Especially under the influence of wind, vibration, dead weight and repeated loads, after a certain service period, the fatigue strength of the outdoor steel structure is reduced due to the corrosion of the component surface and other reasons[9,10]. Abnormal damage may occur and result in unpredictable accidents and losses.

In recent years, many scholars have performed a great deal of work on the safety of Q345B steel and its outdoor structure. However, most of these works focus on the surface modification of the material and strength of the steel structure, and there are few studies on the corrosion of the potential chloride-ion-polluted environment encountered by the material in the service process[11]. Because the outdoor corrosion of Q345B steel is closely related to the soil media involved, the corrosion behavior of the outdoor steel structure of Q345B steel in different soil environments varies[12-14]. At present, there remains a lack of research on the corrosion characteristics and corrosion laws in simulated real soil and an environment polluted by chloride ions.

In this paper, based on the real soil environment, Q345B steel under chloride ion pollution law of corrosion in soil environment is studied using configuration simulations of solution soak Q345B steel samples. The chloride ion contamination of the samples is determined under open circuit potential, polarization curve, electrochemical impedance spectroscopy(EIS) and immerse mass loss and other data to obtain information about the corrosion rate and corrosion morphology. The rule of corrosion rate of Q345B steel is summarized. The results can provide a reference for corrosion protection and structural design of Q345B steel in a real service environment.

# 2. EXPERIMENTAL METHOD

#### 2.1 Experimental materials

The experimental material is Q345B steel, whose chemical composition is shown in Table 1.

Alloy	С	Si	Mn	S	Р	Cr	Ni	Cu	Fe
% wt	0.15	0.12	1.26	0.021	0.013	0.08	0.16	0.046	balance

Table 1. Chemical compositions of Q345B

# 2.2 Electrochemical Test

The working electrode size of the electrochemical test was Q345B steel with a 10 mm $\times$ 10 mm $\times$ 10 mm. After the sample had been processed, the oil and rust on the surface of the sample were

carefully cleaned. Then, epoxy resin was used for vacuum cold mounting. A magnifying glass was used to check the edge of the sample to prevent the occurrence of gap corrosion, which would expose  $1 \text{ cm}^2$  of the area to be measured. After cold setting, the surface of the sample was polished step by step using 800# water abrasive paper, cleaned with deionized water, rid of residual moisture by anhydrous ethanol, and dried by cold air. Finally, the sample was put into a dryer for later use.

Experimental solution was prepared using the following method: after soil of DeYang area crushing, drying and sieving, according to the soil:the deionized water = 1:5 (mass ratio) was mixed by stirring; the upper clear solution was let stand for 72 h after being divided into two: one was not processed (soil solution), and the other was added a certain amount of NaCl (20 mmol/L, soil solution with 20 mmol/L NaCl). Electrochemical tests were performed on a PARSTAT4000 electrochemical workstation using a conventional three-electrode system. The investigated material (Q345B steel) was used as the working electrode, a platinum plate was used as the auxiliary electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The test temperature was  $23\pm2$  °C.

Before the EIS test, the working electrodes were stabilized at the open circuit potential (OCP, vs. SCE) for 900 s. The final, stable open-circuit potential was recorded. The scanning range of the potentiodynamic polarization test was  $\pm 300$  mV (vs. OCP), and the scanning rate was 0.167 mV/s.

The corresponding electrochemical parameters were measured after the open-circuit test had completed. Electrochemical impedance spectroscopy was measured under a stable open circuit, the frequency test range was  $10^5 \sim 10^{-2}$  Hz, and the AC disturbance voltage was 10 mV. The ZSimpWin software was used to fit and analyze the data.

#### 2.3 Immersion corrosion test

The sample size for the mass loss experiment was  $20 \times 10 \times 50$  mm. The surface of the samples was polished to 800# water abrasive paper step by step. Then, the sample surface was cleaned with deionized water, residual moisture was removed by anhydrous ethanol, and the sample was blown dry usingcold air. Afterwards, the sampleswere placed in a dryer for 24 h and individually weighed (accurate to 0.1 mg). Finally, the samples were divided into two parts and soaked in different soil leaching solutions. The immersion experiment period was 21 days.

The acid washing solution for removing corrosion products from the sample in the mass loss test was composed of 500 mL hydrochloric acid (HCl,  $\rho$ =1.19 g/ml) + 5 g1,3-dibutyl 2-thiourea +500 mL deionized water. After the corrosion products were removed from the acid washing solution, the sample was cleaned with deionized water and anhydrous ethanol and quickly dried with cold air. After standing in a drying dish for 24h, the sample was weighed (accurate to 0.1 mg).The corrosion rate of the material was calculated by Formula (1).

# $R=(M-M_t)/ST$

where R is the corrosion rate( $g/(mm^2 \cdot a)$ ); M is the mass before the experiment; M<sub>t</sub> is the mass after pickling, unit g; S is the sample surface area, unit mm<sup>2</sup>; T is the experiment time, unit a.

(1)

# 2.4 Corrosion morphology and composition analysis

At the end of the experiment, the samples were immediately rinsed with anhydrous ethanol and deionized water and subsequently quickly dried with cold air. Thermo Fisher APREO field emission electron microscopy (FSEM) was used to observe the corrosion microscopic morphology of the working electrode surface; additionally, the composition was measured by energy dispersive spectroscopy(EDS). An OLYMPUS OLS5000 confocal laser microscopewas used to observe the morphology of the corrosion pits.

# **3. RESULTS AND DISCUSSION**



#### 3.1 Open-circuit potential test

Figure 1. Open-circuit potential of Q345B in different solutions

Figure 1 shows the open-circuit potential of Q345B stabilized in the leaching solution for 900 s in different states. In the original soil leaching solution, the final stable open circuit potential was -621 mV. In the soil leaching solution contaminated by 20 mmol/L NaCl, the corresponding material stable open-circuit potential was -645 mV. Hence, 20 mmol/L NaCl pollution leads to a negative shift of 24 mV for the stable open-circuit potential of the material. A more negative open-circuit potential corresponds to greater corrosion tendency of the material in the environment[15,16].

#### 3.2 Potentiodynamic polarization test

Figure 2 shows the potentiodynamic polarization curve of sample Q345B in soil leaching solutions with different NaCl concentrations. The slopes of the cathodic polarization curves of all curves in the figure are very similar, which indicates that the addition of NaCl has no obvious effect on the cathodic polarization of Q345B[17]. In different solutions, the anodic curves are smooth and

without twists and turns, and active dissolution occurs at the anode. The change in chloride ion concentration has no effect on the reaction mechanism of the anode and cathode of Q345B steel. However, the corrosion potential in figure 2 was more negative than the open-circuit potential in figure 1, due to the cathode polarization of the sample in the potentiodynamic polarization test. Figure 2 shows that the corrosion degree of Q345B steel in different soil simulated solutions is different, and no typical passivation zone appears in the polarization curve, which indicates that no effective corrosion product film covers the entire surface of the electrode on Q345B steel, and the metal is in an active and dissolved state[18,19].



Figure 2. Potentiodynamic polarization curves of Q345B in different solutions

When NaCl was added to the soil leaching solution, the polarization curve of Q345B steel shifted to the lower right, the self-corrosion potential ( $E_{corr}$ ) of the working electrode shifted from -734 mV to -752 mV, and the self-corrosion current ( $I_{corr}$ ) increased from 2.794  $\mu$ A by 17.3% to 3.278  $\mu$ A. According to Faraday's second law, a larger  $I_{corr}$  corresponds to a higher corrosion rate. This is due to the appearance of Cl<sup>-</sup> in the soil leaching liquid: corrosive Cl<sup>-</sup> ions increase the spread on the Q345B steel surface, continuously work on the surface of the electrode of the corrosion solution of Fe and Cl<sup>-</sup> in the reaction solution into a higher solubility of iron chloride from the steel surface of the product membrane[20,21], form continuous consumption, and increase thetendency of corrosion and corrosion current.

# 3.3. Electrochemical impedance spectroscopy test

The Nyquist spectrum of Q345B steel in different soil simulation solutions is shown in figure 3. As the figure shows that the impedance spectrum presents a single capacitive arc feature under different chloride ion concentrations. The radius of the capacitive arc can reflect the resistance in the electrochemical process[22].

When there is NaCl in the simulated soil solution, the capacitive arc resistance and corresponding reaction resistance are minimal. This result shows that Q345B steel is more prone to corrosion under this condition. To better explain the above rules, the ZSimpWin software is used to fit

the Nyquist spectrum, and the equivalent circuit is shown in figure 4. In the equivalent circuit,  $R_s$  is the solution resistance, Q is the electrode capacitance, and  $R_t$  is the charge transfer resistance. Because the corrosion products will have a certain roughness on the electrode surface, which will produce a dispersion effect, the constant phase angle element (CPE) is used to replace the pure capacitor element in the equivalent circuit[23].



Figure 3. Electrochemical impedancespectroscopy of Q345B in different solutions



Figure 4. Electrochemical impedance spectroscopy fitting circuit of Q345B in different solutions

In the soil solution without NaCl of Q345B steel, the surface corrosion product film inhibited the diffusion of corrosive ions and the corrosion process of corrosive ions on steel. When NaCl was added to the solution, the resistance of the solution decreased from 437  $\Omega$ •cm<sup>2</sup> to 298  $\Omega$ •cm<sup>2</sup>, and the charge transfer resistance decreased from 1907  $\Omega$ •cm<sup>2</sup> to 1225  $\Omega$ •cm<sup>2</sup> with the minimum charge transfer resistance. The resistance of corrosive ions in the medium decreased, the resistance of the reaction process also decreased, and the corrosion intensified. This is consistent with the polarization curve.

# 3.5 Immersion test

Figure 5 shows the average corrosion rate of Q345B steel after 21 d of immersion in the soil simulation solution. As seen from the figure, when NaCl is added to the solution, the corrosion rate of Q345B steel increases from 0.503 g/(mm<sup>2</sup>•a) to 0.983 g/(mm<sup>2</sup>•a), and the corrosion rate increases by

95.4%, which indicates that the corrosion is aggravated. This result is consistent with the corrosion trend of the polarization curve, but the corrosion degree is higher because the sample has no cathodic polarization during immersion[24].



Figure 5. Average corrosion rate of Q345B in different solutions

3.6 Corrosion morphology



Figure 6. Confocal laser morphology of Q345B in different solutions: (a) soil solution and (b) soil solution with 20 mmol/L NaCl

Figure 6 shows the surface morphology of Q345B steel after soaking in the original solution and NaCl solution for 21 d. In figure 6a, the corrosion morphology of Q345B steel in the original solution shows that in addition to slight scratches on the surface during preparation, many evenly distributed areas with slight corrosion appear on the sample surface, and the corrosion morphology of some areas with serious corrosion presents obvious strip-like corrosion. Pitting corrosion was also observed on the sample surface under scanning electron microscopy (Figure 7a).



**Figure 7.** SEM morphology of Q345B in different solutions: (a) soil solution; (b) soil solution with 20 mmol/L NaCl; (c) corrosion products



Figure 8. Element distribution of Q345B in soil solution: (a) oxygen element; (b) iron element

In the solution with added NaCl, the corrosion of Q345B steel was intensified:a dense strip corrosion area formed, which accounted for the majority of the entire sample area (Figure 6b) and shows a tendency of large area, shallow depth and strip corrosion morphology. However, scanning electron microscopy observations show that the number of pitting corrosions did not significantly increase (Figure 7b).



Figure 9. Element distribution of Q345B in soil solution with 20 mmol/L NaCl solution; (a) oxygen element; (b) iron element

Compared to the two types of corrosion in the solution of the sample, the corrosion of Q345B steel exhibited a color burn area and obvious banded corrosion area, but the lack of significant difference among the sample surfaces indicates that under the condition of the Q345B steel with uniform corrosion, pitting corrosion pits and parts that simultaneously appeared indicate that the samples had slightly uneven corrosion (Figure7). Figure 7c shows the microscopic morphology of corrosion products generated by immersion in the soil simulation solution of Q345B steel. Corrosion products are taken from the sample in figure 6. As shown in figure 7c, the corrosion products are closely bonded flake products of the matrix and stacked together in different directions. There are obvious gaps between the lamellae. The fracture edges of the lamellae are relatively straight, and the surface is smooth.

Figure 8 and 9 show the surface scanning analysis results of the corrosion products randomly selected by EDS. The main elements of the corrosion products are Fe (Figure 8a and Figure 9a) and O (Figure 8b and Figure 9b), which indicates that the corrosion products are mainly Fe oxides[25,26].

When the anions in the solution adsorb on the electrode surface and the metal corrodes, the anodic reaction[27] is as follows (Formula 2):

 $Fe \rightarrow Fe^{2+}+2e$  (2)

In neutral or alkaline soils,  $Fe^{2+}$  further reacts with OH<sup>-</sup> to produce white  $Fe(OH)_2$  (Formula 3):  $Fe^{2+}+2OH^- \rightarrow Fe(OH)_2$  (3)

Fe(OH)<sub>2</sub> generates insoluble Fe(OH)<sub>3</sub> under the combined action of O<sub>2</sub> and H<sub>2</sub>O (Formula 4): 4Fe(OH)<sub>2</sub>+O<sub>2</sub>+2H<sub>2</sub>O $\rightarrow$ 4Fe(OH)<sub>3</sub> (4)

Although  $Fe(OH)_3$  is insoluble, it is not stable and will have the following transformation reaction (Formula 5 and 6):

 $Fe(OH)_3 \rightarrow FeOOH+H_2O$ (5) 8FeOOH+ Fe<sup>2+</sup>+2e $\rightarrow$ 3Fe<sub>3</sub>O<sub>4</sub>+4H<sub>2</sub>O (6)

Combined with figure 2, under the above conditions, Cl<sup>-</sup> plays an activation role in the corrosion reaction process, which intensifies the corrosion of Q345B steel. In the soil, there are generally  $HCO_3^{-}$ ,  $CO_3^{2^{-}}$  and  $HO^{-}$  plasma. The three ions are adsorbed on the surface of the electrode

together as active substances, corrode the surface of part of Q345B and form a stable corrosion product film. The anodic reaction product  $Fe^{2+}$  (Formula 2) combines with the active adsorbent to form unstable products  $Fe(OH)_2$  (see Formula 3) and  $FeCO_3$  (Formula 7 and 8).

 $\begin{array}{ll} Fe^{2+} + HCO_3^{-} \rightarrow FeCO_3 + H^+ & (7) \\ Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 & (8) \\ FeCO_3 \text{ reacts with OH}^- \text{ to form a corrosion product film:} \\ FeCO_3 + 5OH^- \rightarrow Fe_3O_4 + 3HCO_3^{-} + H_2O + 2e & (9) \\ 2FeCO_3 + 4OH^- \rightarrow \gamma - Fe_2O_3 + 2HCO_3^{-} + H_2O + 2e & (10) \end{array}$ 

When there is Cl<sup>-</sup> in the solution, it will compete with anions such as OH<sup>-</sup> in the solution and adsorb on the electrode surface. Increasing the NaCl concentration will lead to more Cl<sup>-</sup> adsorbing on the electrode surface and accelerate the corrosion of the material. However, with the emergence of anionic Cl<sup>-</sup> with a smaller ionic radius, it has a strong penetration ability and easily reaches the metal surface through the tiny pores in the corrosion product film to form iron chloride with higher solubility. Thus, the corrosion potential negatively shifts, and the charge transfer resistance and corrosion rate increase in the electrochemical test[24,28].

Obvious pitting pit features are observed in figure 7a and 7b. Although the presence of NaCl increased the corrosion rate, the corrosion resistance of Q345B decreased, and the weight loss rate was higher than that of the sample in the original soil leaching solution. However, the samples in the original soil leaching solution had similar slight pitting corrosion, so the surface of the samples retained the characteristics of overall corrosion.

# **4.CONCLUSION**

In soil leaching containing Cl<sup>-</sup>, the competitive adsorption of Cl<sup>-</sup> on the electrode surface of Q345B steel will reduce the self-corrosion potential of Q345B steel, improve the corrosion current, reduce the solution resistance and charge transfer resistance of the soil leaching solution, improve the weight loss rate of materials, and promote the corrosion of materials.

The addition of 20 mmol/L NaCl can promote the small radius and strong penetration of Cl<sup>-</sup> to reach the surface of Q345B steel through the pores of the corrosion product membrane to generate corrosion products with higher solubility, increase the number of corrosion active points of Q345B steel, and induce the corrosion to develop from light-colored and pitted corrosion to dark and banded corrosion.

The corrosion product films of Q345B steel that form in different soil leachates are mainly composed of Fe oxides, and the material surface shows the coexistence of overall corrosion and local slight uneven corrosion. Cl<sup>-</sup> has no obvious effect on the formation and development of pitting corrosion in Q345B steel.

# References

- 1. R.C. Battista, R.S. Rodrigues and M.S. Pfeil, J. Wind. Eng. Ind. Aerod., 91 (2003)1051.
- 2. J.Y. Wen and Q. Xie, Eng. Fail. Anal., 117 (2020) 104810.

- 3. Z.F. Alemdar and F. Alemdar, Eng. Fail. Anal., 125 (2020) 105378.
- 4. D.V. Cauteren, D.Ramon, J. Stroeckx, K. Allacker and M. Schevenels, *Energ. Buildings.*, 254 (2022) 111600.
- 5. P. Lehner, V. Křivý, M. Krejsa, P. Pařenica and J. Kozák, Procedia. Struct. Integr., 13 (2018) 1539.
- 6. N. Gowripalan and H.M. Mohamed, Cement . Concrete. Res., 28(1998)1119.
- 7. S.Permeh, K.Lau, M.E. Boan and M. Duncan, Constr. Build. Mater., 274(2021) 122087.
- 8. S.L. Li, L.G. Zhang, Y. Wang, P.Y.Hu, N. Jiang, P. Guo, X.D. Wang and H. Feng, *Structures.*, 29(2021)1655.
- 9. B.J. Dong, W. Liu, T.Y. Zhang, L.J.Chen, Y.M. Fan, T.G. Zhao, W.J.Yang and W. Banthukul, *Eng. Fail. Anal.*, 129(2021) 105720.
- 10. H.J. Wang, Z.W. Zhang, H.L. Qian and F. Fan, Eng. Struct., 224(2020)111205.
- 11. Z.C. Liu, Y. Li, S. Dong and Z.Y. Zhang, Ocean. Eng., 239(2021)109912.
- 12. A. Turnbull and S. Zhou , Corros. Sci., 52(2010) 2936-2944.
- 13. F. Corvo, T. Perez, L.R. Dzib, Y. Martin, A. Castañeda, E. Gonzalez and J. Perez, *Corros. Sci.*, 50(2008)220.
- 14. L.J. Zhou and S.W. Yang, Constr. Build. Mater., 281(2021)122564.
- 15. K. Selvam, J. Saini, G. Perumal, A. Ayyagari, R. Salloom, R. Mondal, S. Mukherjee, H.S. Grewal and H.S. Arora, *Tribol. Int.*, 134 (2019) 77.
- 16. F. Arjmand, L.F. Zhang and J.M. Wang, Nucl. Eng. Dign., 322 (2017) 215.
- 17. X.D. Chen, Y.S. Li, Y.T. Zhu, Y.K. Bai and B. Yang, Appl. Surf. Sci., 481 (2019) 1305.
- 18. D.G. Li, J.D. Wang, D.R. Chen and P. Liang, J. Power Sources., 272 (2014) 448.
- 19. L. Li, C.F. Dong, K. Xiao, J.Z. Yao and X.G. Li, Cons. Build. Mater., 68 (2014) 709.
- 20. T. Pojtanabuntoeng and M. Salasi, *Electrochim. Acta*, 258 (2017) 442.
- A.A. Dastgerdi, A. Brenna, M. Ormellese, M.P. Pedeferri and F. Bolzoni, *Corros. Sci.*, 159 (2019) 108160.
- 22. L. Pan, C.T. Kwok and K.H. Lo, J. Mater. Process. Tech., 277 (2020) 116448.
- 23. O.J. Gerald, L.W. Ge, L. Zhang, Z.Y. Tao and L.C. Long, Mater. Chem. Phys., 239 (2020) 122010.
- 24. D.C. Kong, C.F. Dong, X.Q. Ni, L. Zhang, J.Z. Yao, C. Man, X.Q. Cheng, K. Xiao and X.G. Li, J. *Mater. Sci. Technol.*, 35 (2019) 1499.
- 25. G.Q. Caetano, C.C. Silva, M.F. Motta, H.C. Miranda, J.P. Farias, L.A. Bergmann and J.F. Santosb, *J. Mater. Res. Technol.*, 2019;8(2):1878.
- 26. S.C.Shen, X.L. Song, Q.Z. Li, X.F. Li, R.H. Zhu and G.G. Yang, *Mat. Sci. Eng.A.*, 740-741 (2019) 243.
- 27. R.N. Parkins and S. Zhou, Corros. Sci., 39(1997) 175.
- 28. Y.Y. Li, Z.Z. Wang, X.P. Guo and G.A. Zhang, Corros. Sci., 147 (2019) 260.

© 2022 The Authors. Published by ESG (<u>www.electrochemsci.org</u>). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).