Article

Electrochemical Study of Stainless Steel Anchor Bolt Corrosion Initiation in Corrosive Underground Water

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Abstract: Application of low-nickel stainless steel anchor was one of the economical and effective methods to solve the durability problem of slope engineering. At present, there are scarce reports about corrosion characteristics of low-nickel stainless steel in various underground waters. For investigating the corrosion initiation of stainless steel anchor bolt in corrosive underground water, the effect of SO$_4^{2−}$, HCO$_3^{−}$ and pH value on the corrosion behavior of 201 low-nickel stainless steel was studied via electrochemical methods. As the SO$_4^{2−}$ concentration, HCO$_3^{−}$ concentration or pH value increase, the open circuit potential and polarization resistance increase, while the double-layer capacitance, donor density and passive current density decrease. The results indicate that corrosion is inhibited by SO$_4^{2−}$, HCO$_3^{−}$ and OH$^{−}$ in underground water. In addition, the inhibitive efficiency of SO$_4^{2−}$ and HCO$_3^{−}$ increases with the SO$_4^{2−}$ and HCO$_3^{−}$ concentration.

Keywords: underground water; corrosion; low-nickel stainless steel; passive film

1. Introduction

Steel anchor bolt is widely applied in the high-steep slope in hydropower and transportation fields, as shown in Figure 1a, which can maintain the slopes in stable conditions. However, many anchor bolts were found to be seriously corroded, causing a collapse of slopes, for the corrosive ions in underground waters. Therefore, much attention was given to the durability of steel anchor bolts in the past several decades.

Figure 1. Diagram of anchor in the rock, (a) anchor in good condition and (b) bond failure anchor.

Steel anchor bolts in corrosive environments may degrade in various manners. Stress corrosion cracking (SCC) is one of the main corrosion-induced failure of bolts [1-5]. It occurs when highly stressed steel bolts are exposed to corrosive environments [2], and it was related to hydrogen embrittlement [3-5]. In addition, as shown in Figure 1b, bond failure at the bolt-grout interface is another degradation mode which frequently occurred [6].
Jiang et al. [7] compared the probability of yield failure at the free length to that of bond failure at the bolt-grout interface, and they found that the former was much lower than the latter over time. Xia et al. [6] suggested a predictive model, which was based on the Mohr–Coulomb theory, to estimate the lifetime of rock bolts in corrosive environments considering bond failure. The model can be applied to arrange rational maintenance programs for anchorage structures. Generally, SCC and bond failure were two main failure modes which attracted much attention in the past several decades.

Except for the studies on the failure modes of steel anchorage bolts [1–7], many studies [7–11] also focused on the factors that influence the corrosion behavior and durability of steel anchorage bolts. Divi et al. [8] investigated the effect of temperature on the corrosion properties of different rock bolts and found that severe corrosion was detected for most rock bolts as the temperature reached 90 °C. The effect of thickness of grout cover layer and water–cement ratio of grout on the long-term stabilization of anchored rock slope was reported by Jiang et al. [7]. The results indicated that the lifetime of rock bolts extended with increasing thickness of grout cover layer on the bolt and decreasing water–cement ratio of the grout. The coupled effect of stress and corrosion on the anchorage performance of rock bolts was investigated by Wang et al. [9], and the authors found that the bonding strength of rock bolts was significantly degraded by the increasing working stress and corrosion time. Similar results were reported by Wang et al. [10], and the longer corrosion time could lead to pitting, which reduced the bearing capacity and lifetime of rock bolts. In general, the durability of bolts can be affected by factors such as temperature, material, stress and corrosion time.

The effect of solution composition on the durability of bolts was also investigated in previous studies. Rahman et al. [11] analyzed the corrosion behavior of rock bolts in simulated concentrated water with different anions (chlorides, sulfates, bicarbonates and silicates) and found that the steels in bicarbonate and silicate solution showed the highest and lowest corrosion, respectively. However, some other studies [12,13] suggested that HCO$_3^-$ ions have an inhibitive effect on corrosion. Moreover, the effect of SO$_4^{2-}$ ions on the corrosion behavior of steels is also controversial [14–17]. Some reports [14,15] indicated that SO$_4^{2-}$ can lead to the dissolution of Cr and accelerate corrosion. By contrast, some other reports [16,17] found the SO$_4^{2-}$ can inhibit general corrosion and pitting corrosion. It is worth noting that those studies [11–17] scarcely paid attention to the corrosion behavior of steels in underground waters.

To resist the corrosive anions in underground water, stainless steel anchors can be adopted to substitute for carbon steel anchors and for the higher corrosion resistance of the former. However, from an economic point of view, the cost of stainless steel is substantially higher than that of carbon steel, because of the increasing price of nickel. Taking the corrosion resistance and the expense into consideration, low-nickel stainless steel is an excellent choice for anchor bolt in corrosive underground water. Some previous studies reported that low-nickel stainless steel exhibited similar corrosion resistance compared with traditional 304 stainless steel. Our previous studies investigated the effect of the concentration of Cl$^-$ in the underground water [18] and stains [19] on the corrosion behavior of the 201 low-nickel stainless steels. In the present study, the effect of the concentrations of SO$_4^{2-}$ and HCO$_3^-$, as well as the pH value on the corrosion behavior of the 201 low-nickel stainless steel, was studied in simulated underground water.

2. Materials and Experiments

2.1. Materials

In total, 201 low-nickel stainless steels were adopted as test specimens, the chemical composition of which was (wt.%): 0.082% C, 0.33% Si, 0.12% N, 9.34% Mn, 14.74% Cr, 0.9% Ni, 1.45% Cu, 0.031% P, 0.007% S and Fe. The low-nickel stainless steel was processed into a rectangular sheet, with a size of 20 mm × 100 mm × 1 mm. The specimens were ground with emery papers to NO. 1000, degreased and washed with absolute ethyl alcohol and deionized water, respectively. Then, the samples were sealed with silica gel, leaving
an area of 0.5 cm\(^2\) in the middle of the geometry exposed for electrochemical tests. The edge between the exposed stainless steel and silica gel were daubed nail enamel after the silica gel cured, to avoid the crevice corrosion. Underground water was prepared with analytic reagent sodium chloride, sodium sulfate and sodium bicarbonate to simulate the underground water of the North Mountain in Gansu Province, China [20]. In addition, for investigating the influence of SO\(_4^{2-}\), HCO\(_3^-\) and pH value on the corrosion initiation of low-nickel stainless steel in underground water, different SO\(_4^{2-}\), HCO\(_3^-\) concentration and pH value were tested, as shown in Table 1. To obtain certain pH values in Table 1, diluted nitric acid was applied, since the nitrate ions have little effect on the corrosion behavior of stainless steel [21].

Table 1. The concentration of various ions in the simulated underground water solution.

| Solution | A1 | A2 | A3 | A4 | A5 | B1 | B2 | B3 | B4 | B5 | C1 | C2 | C3 |
|----------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Cl\(^-\) (g/L) | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 |
| SO\(_4^{2-}\) (g/L) | 2.75 | 5.50 | 11.00 | 22.00 | 44.00 | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 | 11.00 |
| HCO\(_3^-\) (g/L) | 1.40 | 1.40 | 1.40 | 1.40 | 1.40 | 0.35 | 0.70 | 1.40 | 2.80 | 5.60 | 1.40 | 1.40 | 1.40 |
| pH | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 5.0 | 7.0 | 9.0 |

2.2. Experiments

Electrochemical measurements were performed via CS350 workstation (Corrtest Instrument, China). The 201 low-nickel stainless steel sample, a platinum plate and a saturated calomel electrode (SCE) was connected to the working electrode, counter electrode and reference electrode, respectively. Three samples were measured in each electrochemical test, and the middle curve was selected to represent the result. Specimens were cathodically polarized at \(-1.0\) V\(_{ \text{SCE} }\) for 5 min before the experiments [22], to remove the oxide film formed in air. One hour after the cathodically polarization, electrochemical measurements were conducted in underground water solutions. The open-circuit potential (OCP) was recorded for 300 s until a stable potential was reached. The average values of three parallel samples were calculated and represented the OCP value in the corresponding conditions. Subsequently, electrochemical impedance spectroscopy (EIS) was measured by applying a 10 mV AC disturbance signal, in the range from \(10^{5}\) to \(10^{-2}\) Hz. Thereafter, Mott–Schottky measurements were conducted at a frequency of 1000 Hz, from \(-1.5\) to \(1.5\) V\(_{ \text{SCE} }\) with 10 mV amplitude signal and a potential step of 50 mV [23–25]. Furthermore, potentiodynamic polarization curves were tested at a scanning rate of 1 mV/s from \(-0.3\) to \(1.1\) V\(_{ \text{SCE} }\) [26], after the stainless steel was immersed in underground water one hour, with three new samples in each condition.

3. Results and Discussion

3.1. Open-Circuit Potential

The OCP values of the 201 low-nickel stainless steel samples in the underground water with different SO\(_4^{2-}\) content, HCO\(_3^-\) content and pH value were presented in Figure 2. As can be seen in Figure 2a,b, the OCP generally slightly shifted to a positive direction with increasing SO\(_4^{2-}\) concentration and HCO\(_3^-\) concentration, suggesting the decrease tendency of corrosion on the 201 stainless steels. Hong [16] investigated the effect of SO\(_4^{2-}\) ions concentration on the early stages of pitting corrosion of 430 stainless steel in NaCl solution and found that the number of metastable pits decreased with increasing SO\(_4^{2-}\) concentration. In addition, Li [12] reported that the corrosion potential increased with increasing HCO\(_3^-\) concentration. These reports confirmed that SO\(_4^{2-}\) ions and HCO\(_3^-\) ions can serve as an inhibitor of chloride-induced corrosion for stainless steels. Furthermore, as shown in Figure 2c, the OCP increased with the pH values. Similar results were reported by Luo [27], that the corrosion resistance of 316 L stainless steel was enhanced by the higher pH values when it was less than 12.5. Therefore, the OCP results suggested that as
the SO$_4^{2-}$ concentration, HCO$_3^-$ concentration and pH values increased, the OCP of the 201 low-nickel stainless steel increased, while its corrosion tendency decreased.

3.2. Electrochemical Impedance Spectroscopy

The Nyquist plots of the stainless steels in the underground water with different SO$_4^{2-}$ and HCO$_3^-$ concentration and different pH value are presented in Figure 3. According to previous studies, the radius of the arc in Nyquist plots is closely related to the polarization resistance [28,29], which usually represents the corrosion resistance of steels. The radius of the arc significantly increased with the increase in SO$_4^{2-}$ concentration, HCO$_3^-$ concentration and pH values, indicating an enhanced corrosion resistance of steels.

The equivalent circuit shown in Figure 3c was applied to fit the EIS data, in which $R_s$ represents the solution resistance, and $Q$ and $R_{ct}$ represent the double-layer capacitance and the charge transfer resistance, respectively [30]. In the present study, constant phase element (CPE) is used in place of pure capacitance, and the impedance of CPE ($Z_{CPE}$) can be given by:

$$Z_{CPE} = \left[Q(j\omega)^n\right]^{-1}$$  \hspace{1cm} (1)

where $n$ is the CPE exponent and $\omega$ is the phase angle frequency. The capacitance element $Q$ (CPE) is pure capacitance when $n = 1$ and pure resistance when $n = 0$. 

![Figure 2](image-url)
The fitting results of charge transfer resistance $R_{ct}$ and double-layer capacitance $Q$ were shown in Table 2 and Figure 4. Generally, with the increase in SO$_4^{2-}$ concentration, HCO$_3^-$ concentration and pH values, the charge transfer resistance $R_{ct}$ increased, while the double-layer capacitance $Q$ decreased. Particularly, the $R_{ct}$ of the sample in the pH 9 solution was one order of magnitude larger than that of the one in the pH 5 solution, which means the corrosion resistance of the 201 low-nickel stainless steel was significantly enhanced in alkaline environment. In addition, as the SO$_4^{2-}$ concentration increased from 2.75 to 22 g/L, the $R_{ct}$ increased to about 2.5 times. Similarly, as the HCO$_3^-$ concentration increased from 0.35 to 2.8 g/L, the $R_{ct}$ increased to about 1.5 times. These situations indicate that the SO$_4^{2-}$ and HCO$_3^-$ exhibited inhibitive effect on corrosion of the 201 low-nickel stainless steel in simulated underground waters. However, when the SO$_4^{2-}$ concentration exceeded 22 g/L or the HCO$_3^-$ concentration exceeded 2.8 g/L, the growth rate of $R_{ct}$ obviously slowed down, which indicates that the corrosion resistance of stainless steel was not further improved by the increase in SO$_4^{2-}$ and HCO$_3^-$ concentration, when they were higher than certain values.
Table 2. The fitting results of EIS data.

| Solution | A1  | A2  | A3  | A4  | A5  | B1  | B2  | B3  | B4  | B5  | C1  | C2  | C3  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $R_s$ (Ω cm$^2$) | 22.4 | 16.4 | 18.2 | 18.0 | 9.52 | 15.9 | 17.3 | 18.2 | 16.3 | 14.7 | 16.9 | 18.2 | 11.2 |
| $R_{ct}$ ($\times 10^5$ Ω cm$^2$) | 1.3 | 1.7 | 2.3 | 3.3 | 4.2 | 2.1 | 2.1 | 2.3 | 3.1 | 3.3 | 0.65 | 2.3 | 5.4 |
| $Q$ ($\times 10^{-5}$ Ω$^{-1}$ S$^n$ cm$^2$) | 6.2 | 6.0 | 5.9 | 5.0 | 4.9 | 5.8 | 5.0 | 5.9 | 4.9 | 4.0 | 9.6 | 5.9 | 6.3 |

Figure 4. Fitting charge transfer resistances ($R_{ct}$) and double-layer capacitance ($Q$) of the 201 stainless steel in the underground water with different contents of $SO_4^{2-}$, $HCO_3^-$, as well as different pH, (a,b) $R_{ct}$ and $Q$ in A1–A5 solutions with different concentration of $SO_4^{2-}$, (c,d) $R_{ct}$ and $Q$ in B1–B5 solutions with different concentration of $HCO_3^-$, and (e,f) $R_{ct}$ and $Q$ in C1–C3 solutions with different pH values.
The capacitance $C$ (i.e., $Q$) is in inverse proportion to the thickness ($d$) of the passive film [31,32]:

$$C = (\varepsilon_0 \varepsilon S)/d \quad (2)$$

where $\varepsilon_0$ is the dielectric constant of free space and $\varepsilon$ is the dielectric constant of the passive film. As shown in Figure 4, with increasing $\text{SO}_4^{2-}$ concentration, $\text{HCO}_3^-$ concentration and pH values, the capacitance decreased, and the thickness of the passive film correspondingly increased, which means the corrosion resistance was enhanced. The EIS results, together with the OCP results, confirmed that the corrosion of the 201 low-nickel stainless steel was inhibited by $\text{SO}_4^{2-}$ and $\text{HCO}_3^-$ in the $\text{Cl}^-$ contaminated underground water and also by the alkaline environment. Moreover, the excessive addition of $\text{SO}_4^{2-}$ and $\text{HCO}_3^-$ seems to have little effect on the improvement of corrosion resistance.

### 3.3. Semiconducting Properties of the Passive Film

Figure 5 shows the Mott–Schottky plots of the 201 low-nickel stainless steels in simulated underground water with different anion concentrations and pH values. Positive slopes can be observed in the Mott–Schottky plots when the potential is in the range of $-0.4$ to $0.2$ V$_{SCE}$, which indicates that the passive film on the stainless steel is an n-type semiconductor [33,34]. However, as the potential exceeds $0.2$ V$_{SCE}$, the slopes turn negative, indicating the initial breakdown of the passive film [35,36].

![Mott–Schottky plots](image)
Assuming that the capacitance of the Helmholtz layer \( C_H \) can be neglected [37,38], the capacitance of n-type semiconductors can be calculated by Equation (3) [34,35]:

\[
C^{-2} = C_{SC}^{-2} = \frac{2}{\varepsilon \varepsilon_0 q N_D} \left( E - E_{FB} - \frac{kT}{q} \right)
\]

where \( C_{SC} \) is the capacitance of space charge layer; \( \varepsilon_0 \) (8.85 \times 10^{-14} \text{ F/cm}) and \( \varepsilon \) (12 [37,38]) are the dielectric constants of the vacuum and the passive film, respectively; \( q \) is the electron charge \( (1.602 \times 10^{-19} \text{ C}) \); \( N_D \) is the donor density of the passive film; \( E \) is the applied potential; \( E_{FB} \) is the flat band potential; \( k \) is the Boltzmann constant \( (1.38 \times 10^{-23} \text{ J/K}) \); and \( T \) is the absolute temperature and in the present study is 295 K. The value of \( kT/q \) is negligible because it is only 25 mV [39,40]. The donor density \( N_D \) of passive films formed in underground water with different anion concentration, and the pH value was obtained from the slopes of Mott–Schottky plots, and the results were presented in Table 3 and Figure 6. As the \( \text{SO}_4^{2-} \) concentration increased from 2.75 to 22 g/L, or the \( \text{HCO}_3^- \) concentration increased from 0.35 to 2.8 g/L, the donor density sharply decreased by more than half. However, when the \( \text{SO}_4^{2-} \) concentration exceeded 22 g/L, or the \( \text{HCO}_3^- \) concentration exceeded 2.8 g/L, the donor density seemed to decline at a slower rate. According to the point defect model (PDM) proposed by Macdonald et al. [41–43], the decrease in donor density suggests the higher stability of the passive film and less susceptible to pitting corrosion. Therefore, the results in Figure 6a,b suggested that the stability of the passive film and resistance to pitting corrosion were enhanced by the increasing of \( \text{SO}_4^{2-} \) and \( \text{HCO}_3^- \), while excessive addition of \( \text{SO}_4^{2-} \) and \( \text{HCO}_3^- \) only led to slight improvement on the stability of the passive film. In Figure 6c, it can be observed that the donor density of the film formed in alkaline environment was much lower compared to that of the film formed in neutral or acidic solutions, which means the stability of the film was substantially improved and the probability of pitting was significantly reduced in alkaline underground water.

In general, the Mott–Schottky results together with the EIS and OCP results, suggested that corrosion of the 201 low-nickel stainless steel was inhibited by the \( \text{SO}_4^{2-} \) and \( \text{HCO}_3^- \) in underground waters. Moreover, the passivity of the low-nickel stainless steel was substantially improved in the alkaline underground waters.

### Table 3. The donor densities of passive film formed on 201 low-nickel stainless steel in different solutions.

| Solution | A1 | A2 | A3 | A4 | A5 | B1 | B2 | B3 | B4 | B5 | C1 | C2 | C3 |
|----------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| \( N_D \times 10^{20} \text{ cm}^{-3} \) | 3.22 | 2.44 | 1.85 | 1.50 | 1.33 | 4.48 | 2.84 | 1.85 | 1.95 | 1.23 | 4.94 | 1.85 | 1.10 |

### 3.4. Potentiodynamic Polarization

The potentiodynamic polarization curves of the samples immersed in underground water with different anion concentrations and pH values were depicted in Figure 7. It can be observed that most stainless steels samples displayed typical passivation state in these underground waters, except for the sample in the solution containing 2.75 g/L \( \text{SO}_4^{2-} \). Furthermore, the passive current densities derived from the potentiodynamic polarization curves were presented in Table 4 and Figure 8. As Figure 8 shows, the current density of the low-nickel stainless steels decreased with increasing \( \text{SO}_4^{2-} \) and \( \text{HCO}_3^- \) in the underground water, especially when the \( \text{SO}_4^{2-} \) concentration was lower than 22 g/L or the \( \text{HCO}_3^- \) concentration was lower than 2.8 g/L. For instance, the passive current density of the sample in the solution with 22 g/L \( \text{SO}_4^{2-} \) was one order of magnitude lower than the one in the solution with 2.75 g/L \( \text{SO}_4^{2-} \). However, when the \( \text{SO}_4^{2-} \) or \( \text{HCO}_3^- \) concentration was higher than certain values, the current density almost remained constant. In addition, the current density of the sample in neutral or alkaline solution was one order of magnitude lower than the one in acidic solution. Lower current density represents the reduction of activity of the low-nickel stainless steel substrate. Thus, the potentiodynamic polarization results confirmed that the corrosion resistance of 201 low-nickel stainless steel increased with increasing \( \text{SO}_4^{2-} \) concentration and \( \text{HCO}_3^- \) concentration. Furthermore,
the stainless steel sample showed higher corrosion resistance in the alkaline underground waters, which concurred with the OCP, EIS and Mott–Schottky results.

Table 4. The passive current density of 201 low-nickel stainless steel in different solutions.

| Solution | A1 | A2 | A3 | A4 | A5 | B1 | B2 | B3 | B4 | B5 | C1 | C2 | C3 |
|----------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| IPass (×10^{-6} A cm^{-2}) | 58.8 | 2.92 | 2.38 | 1.97 | 1.69 | 4.58 | 3.69 | 2.38 | 1.12 | 0.950 | 46.4 | 2.38 | 4.80 |

Figure 6. Influence of compositions on N_D in the passive films of the low-nickel stainless steel in groundwater solution, (a) A1–A5 solutions with different concentration of SO\textsubscript{4}\textsuperscript{2-}, (b) B1–B5 solutions with different concentration of HCO\textsubscript{3}-, and (c) C1–C3 solutions with different pH values.

Figure 7. Conts.
3.5. The Corrosion Initiation of Stainless Steel in Underground Water

The OCP, EIS, Mott–Schottky plot and potentiodynamic polarization results reveal that corrosion and pitting corrosion can be inhibited by the \( \text{SO}_4^{2-} \), \( \text{HCO}_3^- \) and alkaline environment. Moreover, the inhibitive effect of \( \text{SO}_4^{2-} \) and \( \text{HCO}_3^- \) is significant at low concentration (for \( \text{SO}_4^{2-} \), it is less than 22 g/L, and for \( \text{HCO}_3^- \), it is less than 2.8 g/L) while ineffectiveness at higher concentration. Thus, \( \text{SO}_4^{2-} \) and \( \text{HCO}_3^- \) are not the aggressive anions for the low-nickel stainless steels in the simulated underground water in the present study.
According to PDM [41–43], passivity breakdown derives from cation vacancy condensation, which may further evolve into pitting corrosion under certain conditions. The cation vacancies result from absorption of aggressive anions (Cl\(^{-}\)) into oxygen vacancies at film/solution interface [34,43]. Excess cation vacancies flux across the passive film and condensate at the metal/film interface, causing separation of the passive film from metal substrate and preventing further growth of the film in the cation vacancy condensation regions [34,35,43]. Considering the continual dissolution of passive film at the film/solution interface, the film over the condensate becomes thinner and eventually breaks down [34,43]. Thus, corrosive solution can penetrate into the condensate, and a micropit (metastable pit) is initiated [45]. The formation of micropit is inseparable from aggressive anions, such as Cl\(^{-}\) in the underground water [20]. In a previous study [18], the corrosion behavior of low-nickel stainless steels was investigated in underground water with different Cl\(^{-}\) concentration. The results suggested that the stainless steel was more severely degraded in underground water with high chloride ion concentration. Therefore, the corrosion of stainless steel can be initiated by Cl\(^{-}\) in the underground water.

In addition to the facilitation of Cl\(^{-}\) to the corrosion initiation, other ions, such as SO\(_4^{2-}\), HCO\(_3^{-}\) and OH\(^{-}\), also have an impact on the corrosion initiation of steels. The electrochemical measurement results in the present study indicate that SO\(_4^{2-}\) has the ability to inhibit corrosion, which can be attributed to the competitive adsorption of SO\(_4^{2-}\) and Cl\(^{-}\) on the steel surface [44–47]. It is that the SO\(_4^{2-}\) is preferentially adsorbed onto the film/solution interface for its higher charge in comparison to Cl\(^{-}\), thus preventing Cl\(^{-}\) from contact with the passive film and reducing the probability of Cl\(^{-}\) absorbed into oxygen vacancy. Therefore, the probability of cation vacancy condensation is reduced, and corrosion can be inhibited. The inhibitive effect of HCO\(_3^{-}\) can also be partially attributed to the competitive adsorption [13]. In addition, the presence of HCO\(_3^{-}\) promotes the formation of protective FeCO\(_3\) film [13] and dilutes the concentration of Cl\(^{-}\) in the micropit [48], inhibiting the nucleation of a stable pit. In the present study, corrosion was also inhibited by the alkaline environment, which could be related to the facilitation of OH\(^{-}\) on passivation [49,50]. It is worth mentioning that the OH\(^{-}\) can be induced by the addition of SO\(_4^{2-}\) and HCO\(_3^{-}\), according to the Equations (4) and (5), which also may contribute to the inhibition effect of SO\(_4^{2-}\) and HCO\(_3^{-}\) on the 201 low-nickel stainless steel in the underground waters.

\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \Leftrightarrow \text{HSO}_4^{-} + \text{OH}^{-} \quad (4)
\]

\[
\text{HCO}_3^{-} \Leftrightarrow \text{CO}_2 + \text{OH}^{-} \quad (5)
\]

In some previous studies [11,14,15], SO\(_4^{2-}\) and HCO\(_3^{-}\) were found to be detrimental to steels. Qiu [14] and Zhu [15] investigated the effect of SO\(_4^{2-}\) on the corrosion of 316L stainless steel and Ni-Mo-Cr alloy (GH3535) in FLiNaK molten salt, respectively. The results suggested that SO\(_4^{2-}\) accelerates the corrosion of both types of steel. The authors attributed this situation to the dissolution of Cr in molten salt with high SO\(_4^{2-}\) concentration. However, in the present study, the ambient temperature of underground water solution (20 °C) was much lower than that of molten salt (700 °C), so that the dissolution of Cr may be insignificant in the underground water. In addition, Rahman et al. [11] reported that A607 steel was obviously corroded in simulated Yucca Mountain water solution with 20 g/L HCO\(_3^{-}\). It seems that HCO\(_3^{-}\) is one of the most aggressive anions in Yucca Mountain underground water. However, in the present study, HCO\(_3^{-}\) was tested in the range from 0.35 to 5.6 g/L, which is much lower than 20 g/L. A previous study [12] suggested that HCO\(_3^{-}\) has an inhibitive effect on corrosion at low concentration, but the inhibitive effect reduces in a solution with high HCO\(_3^{-}\) concentration. Generally, the effect of SO\(_4^{2-}\) and HCO\(_3^{-}\) on corrosion behavior of steels could be changed with the solutions or the types of steels. In the present study, SO\(_4^{2-}\) and HCO\(_3^{-}\) seem to be corrosion inhibitors for the low-nickel stainless steels in chloride-contaminated underground water.
4. Conclusions

In the present study, the corrosion initiation of 201 low-nickel stainless steel was studied in simulated underground water with various anions concentration. The following conclusions can be drawn from the results.

1. The open-circuit potential and charge transfer resistance increase, while the double-layer capacitance, donor density and passive current density decrease as the $\text{SO}_4^{2-}$ concentration, $\text{HCO}_3^-$ concentration or pH value of the underground water increase.

2. The corrosion of 201 low-nickel stainless steel is inhibited by $\text{SO}_4^{2-}$, $\text{HCO}_3^-$ and $\text{OH}^-$ in underground water.

3. The inhibitive effect of $\text{SO}_4^{2-}$ and $\text{HCO}_3^-$ is significant at low concentration (for $\text{SO}_4^{2-}$, it is less than 22 g/L, and for $\text{HCO}_3^-$, it is less than 2.8 g/L), while the excessive addition of $\text{SO}_4^{2-}$ and $\text{HCO}_3^-$ only showed a little improvement on the corrosion resistance of 201 low-nickel stainless steel.

4. The passivity and corrosion resistance of low-nickel stainless steel is substantially improved in alkaline underground waters.

5. Anion concentrations was magnified in simulated underground waters in the present study. Corrosion behavior of 201 low-nickel stainless steel in underground waters with lower concentration of anions, and the relationship between corrosion rates in the simulated solution and that in actual groundwater environment should be investigated in the future study.

Author Contributions: Conceptualization, F.M. and Q.Z.; methodology, F.M.; software, T.W.; validation, X.L. (Xiao Lu) and T.Z.; formal analysis, T.W.; investigation, X.L. (Xiangyu Lu); resources, X.F.; data curation, X.L. (Xiao Lu); writing—original draft preparation, F.M.; writing—review and editing, Q.Z.; visualization, X.L. (Xiangyu Lu); supervision, X.F.; project administration, T.W.; funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by The Sichuan Science and Technology Program “Research and application of high-efficiency natural gas production technology from renewable energy based on high-temperature solid oxide electrolyzer cell (2020YFG0314)”.

Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Conflicts of Interest: The authors declare no conflict of interest.

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