



# Article Electrochemical Investigation of Chloride Ion-Induced Breakdown of Passive Film on P110 Casing Steel Surface in Simulated Pore Solution: Behavior and Critical Value Determination

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Abstract: In the petroleum industry, the casing steel is fixed with a cement sheath to ensure reliable service in demanding conditions characterized by high temperature, high pressure, and exposure to multiple types of media. After the hydration of the cement, a porous material is produced with a highly alkaline solution filling the pores, commonly referred to as the pore solution. The casing will form a protective passive film when in contact with a highly alkaline pore solution. Nevertheless, once the cement sheath cracks, chloride ions in the stratum will pass through the cement sheath to the surface of the casing. When chloride ions accumulate to a certain concentration, the passive film will be destroyed, without exerting a protective influence on the substrate. After chloride ions come into direct contact with the casing, the casing is prone to severe failure due to corrosion perforation. The casing failure can cause a blowout outside the casing and even scrapping of the oil well. Controlling casing corrosion and ensuring casing integrity relies on understanding the critical chloride ion concentration that can cause the degradation of the passive film. Therefore, to assess the electrochemical properties and analyze the damage process of the passive film under varying chloride ion concentrations, several characterization techniques were employed. These included potential-time curves (E-t), polarization curves, electrochemical impedance spectroscopy (EIS), and Mott-Schottky curves. In addition, the composition of the passive film on the surface of the P110 casing steel was qualitatively analyzed using X-ray photoelectron spectroscopy (XPS). To further understand the surface morphology of the P110 casing steel, scanning electron microscopy (SEM) was used.

**Keywords:** casing steel; alkaline simulated pore solution; passive film; chloride ion; electrochemical; XPS

## 1. Introduction

The surface of an underground casing is sealed with a cement sheath, and after hydration and solidification, the cement will present a porous form. Due to the high alkali solution (pH  $\approx$  12.5) in the small pores of cement, a dense passive film is formed on the casing steel surface. This formation contributes to excellent corrosion resistance of the casing [1–5]. However, in a complex underground environment, with higher temperature and pressure than on the ground and exposure to different media, and with time or cracking of the cement, water and chloride ions from outside penetrate the cement sheath and reach the interface between the cement sheath and the casing steel. This causes a decrease in



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). pH in the medium environment, a potential for a negative shift in the casing corrosion, and a change to an active dissolution state. When the passive film is damaged, it leads to corrosion or even perforation failure of the casing, causing huge economic losses [6].

Chloride ions can reach the interface between the cement and the casing steel through the cement protective layer and gradually accumulate at the interface. As the concentration of chloride ions near the casing surface gradually rises, it eventually reaches a critical threshold. Chloride ion action may cause local passive film breakdown and corrosion on the casing steel [7–9]. The chloride threshold level that triggers the corrosion of casing steel can be defined as the minimum chloride ion content that promotes the decomposition of local passive film on the casing steel under highly alkaline conditions of the cement sheath [10–13]. Having an insignificant ionic radius and strong penetrability, chloride ions can penetrate the produced oxide film and reach the surface of the metal substrate. Subsequently, this can promote the hydrolysis of  $Fe^{3+}$  to generate  $H^+$ , thus promoting the electrochemical corrosion of the metal substrate. Chloride ions can induce and promote local metal corrosion, such as pitting and crevice corrosion, causing significant damage to the metal. Khaled et al. [14] studied the corrosion performance of carbon steel with supersonic flame spray coating in a simulated pore solution containing chloride ions. In the absence of coating, carbon steel exhibited severe corrosion, mainly pitting corrosion. Ghods et al. [15] studied the changes in the composition of passive films on carbon steel in a simulated pore solution containing chloride ions. Nahali et al. [8] investigated the effect of inhibitors on the chloride threshold in saturated hydroxide solutions. Domestic studies have also investigated the impact of chloride ions on the passivation of steel in simulated pore solutions. Ye et al. [7] used electrochemical methods such as electrochemical impedance spectroscopy (EIS) to discuss the critical concentration of chloride ions resulting in damage to the passive film in a simulated pore solution. The invasion of chloride ions disrupts the stability of the passive film and weakens its corrosion resistance. Meanwhile, the density of the passive film decreases due to the deposition of many loose grains.

There are generally two mechanisms in which chloride ions cause damage to the passive film, as shown in Reactions (1-2). The mechanism expressed in Reaction (1) is that chloride ions having a small radius and strong permeability easily interact with metals to form soluble chloride through tiny pores in the film. This leads to damage to the passive film and pitting corrosion. A sufficient electric field is key in damaging the passive film. The intensity of the induced electric field depends on the concentration of chloride ions and the electrode potential. Therefore, the destruction of the membrane requires a minimum chloride ion concentration (critical concentration) and a minimum potential (pore corrosion breakdown potential), as well as a longer incubation period. Adsorption theorists believe that the fundamental reason for the destruction of the passive film by chloride ions is that chloride ions have a strong ability to be adsorbed by metal, and that the interaction between chloride ions in solution and dissolved oxygen or  $OH^-$  occurs. As shown in Reaction (2), owing to the competitive adsorption on the metal surface, the dissolved oxygen previously adsorbed on the weak points of the passivation film is replaced by chloride ions, converting the passivation film with excellent corrosion resistance into a soluble complex, resulting in damage to the oxide film and local corrosion [16].

$$Fe^{3+}_{pas} + 3Cl^- \rightarrow FeCl_3$$
 (1)

$$FeCl_3 \to Fe^{3+}{}_{sol} + 3Cl^- \tag{2}$$

This article mainly conducts in-depth research on the damage of the chloride ion concentration to the passivation film through electrochemistry and surface analysis. It explores the decisive role of critical chloride ion concentration in corrosion, providing a reference for future research.

## 2. Experimental

## 2.1. Materials and Environment

Table 1 presents the chemical composition (wt.%) of the P110 steel used in the experiment. The plate specimens were machined in a length, width, and height of 10 mm, 10 mm, and 3 mm, respectively. Before testing, all samples were pre-treated. The sample surface was polished using 1000-mesh silicon carbide paper and thoroughly cleaned with acetone.

Table 1. Chemical composition (wt.%) of P110 steel.

С	Si	Mn	Р	S	Cr	Мо	Ni	V	Ti	Cu	Fe
0.25	0.20	1.40	< 0.009	< 0.003	0.15	0.01	0.012	0.012	0.030	< 0.01	Bal.

Previous studies have shown that pH is less than 13, and the experimental material is the G-grade Portland cement prepared by China Jiahua Enterprise Co., Ltd. The cement has the following mineral composition: 64.77% CaO, 22.43% SiO<sub>2</sub>, 4.76% Al<sub>2</sub>O<sub>3</sub>, 4.10% Fe<sub>2</sub>O<sub>3</sub>, 1.14% MgO, 0.24% Na<sub>2</sub>O (K<sub>2</sub>O), and 1.67% SO<sub>3</sub> [17]. The simulated pore solution in this article was prepared by mixing analytical grade reagents with distilled water to obtain a solution containing 0.19 M of NaOH and 0.02 M of Ca(OH)<sub>2</sub>, with a pH of 12.5. Before the experiment, the solution was completely deoxygenated by injecting N<sub>2</sub>. NaCl with different concentrations (0.1 mol/L, 0.15 mol/L, 0.16 mol/L, and 0.2 mol/L) was added to the simulated pore solution to study passive membrane destruction. The experiment was conducted in a water bath with a temperature of 65 °C.

#### 2.2. Electrochemical Measurements

A three-electrode system, shown in Figure 1, consisting of a working electrode, reference electrode, and counter electrode, was employed to conduct electrochemical experiments. The experiments could give rise to electrochemical behavior that depends on electrochemical synthesis instruments (Autolab Model PGSTAT302N, Metrohm AG, Herisau, Switzerland). A steel sample served as the working electrode, with only 10 × 10 mm<sup>2</sup> of the surface exposed to the solution. A circular Pt electrode surrounding the sample was used as the counter electrode, while the Ag/AgCl electrode in a saturated KCl solution was the reference electrode. Firstly, an open circuit potential test was conducted at an AC voltage with an amplitude of  $\pm 10$  mV. Then, electrochemical impedance spectroscopy (EIS) measurements were performed based on the open circuit potential, ranging from 10 mHz to 100 kHz. Finally, polarization tests were conducted sequentially, with a scanning speed of 1.5 mV/s and a scanning range of  $\pm 25$  mV. Each group of tests was conducted three times to reduce errors. In addition, the Mott–Schottky measurements required maintaining a frequency of 1 kHz and a scanning rate of 10 mV/s.

## 2.3. Material Characterization

X-ray photoelectron spectroscopy (XPS) measurements were carried out through an XSAM800 XPS instrument (Kratos, Manchester, UK) to analyze the characteristics of the P110 steel surface films. The specific parameters are as follows: XPS survey spectra: 150 eV of Pass Energy, and 1.0 eV of Energy Step Size; high-resolution XPS spectra: 50 eV of Pass Energy, 0.05 eV of Energy Step Size. Calibration: C-C: 285 eV. The microstructure of the film damaged by chloride ions in this study was observed using a ZEISS EVO MA15 scanning electron microscope (Carl Zeiss AG, Jena, Germany). The method was supported by electron beams accelerated using a constant potential that excited the specimen surface. The interactions between these primary electrons and the specimen resulted in the release of secondary, backscattered X-rays and Auger electrons.



Figure 1. The three-electrode system.

## 3. Results and Discussion

3.1. Determination of Steady-State Passivation Time

The stabilizing potential means that the passive film reaches a state of complete passivation and maintains a dynamic equilibrium. The potential–time relationship of P110 steel in a simulated pore solution is depicted in Figure 2. Overall, the corrosion potential showed an upward trend over time and the behavior could be categorized into three distinct stages. The potential increased rapidly in the first stage and slowly in the second stage, stabilizing in the third stage for 16 h. The oxide film was formed at the interface between the solution and steel, continuously thickening over time. When the thickness of the oxide film no longer increased with time, the potential stabilized, increasing the resistance of the P110 steel dissolution reaction. Therefore, the sample was immersed in a simulated pore solution for 16 h for chloride ion destruction experiments.



Figure 2. Potential-time curve of P110 steel in simulated pore solution.

#### 3.2. Electrochemical Behavior of Chloride Ions in Depassivation

The detrimental effect of chloride ions on the passive film can be attributed to irreparable complete damage. However, before reaching a certain concentration, chloride ions can hardly penetrate the passive film to cause corrosion to the metal substrate. At the oxide film/solution interface, chloride ions adsorb and interact with the oxide film, thinning the passive film. Under a high electric field, the adsorbed chloride ions with a small radius can pass through the passive film and migrate towards the interface between the film and metal, resulting in oxide film breakdown and matrix dissolution [18]. The dissolution of the metal matrix involves the chemical reactions shown in Reactions (3)–(8). The process is that the metal loses electrons to form a divalent iron ion.  $Cl^-$  reacts with  $OH^-$  and  $Fe^{2+}$  to form soluble chlorides and  $FeOH^+$ , and soluble chlorides and  $FeOH^+$  react with  $OH^-$  and  $Cl^-$  to form Fe(OH)Cl. Under alkaline conditions, Fe(OH)Cl reacts with  $OH^-$  to form  $Fe(OH)_2$ . As the concentration of  $Cl^-$  or  $OH^-$  increases, the corrosion of iron also increases.

$$Fe \to Fe^{2+} + 2e^- \tag{3}$$

$$Fe^{2+} + OH^- \to FeOH^+$$
 (4)

$$Fe^{2+} + Cl^- \to FeCl^+ \tag{5}$$

$$FeOH^+ + Cl^- \to Fe(OH)Cl$$
 (6)

$$FeCl^+ + OH^- \rightarrow Fe(OH)Cl$$
 (7)

$$Fe(OH)Cl + OH^- \rightarrow Fe(OH)_2 + Cl^-$$
 (8)

The  $[OH^-]/[Cl^-]$  ratio can be used to measure whether the passive film is damaged [19,20]. Saremi et al. [21] provided a  $[OH^-]/[Cl^-]$  value and found that chloride ions with a critical concentration of approximately 0.6 could correspond to it. Provided that this conclusion is also applicable to the experiment, the critical concentration of obtained chloride ions can reach about 0.138 mol/L.

The potential-time curve aims to preliminarily determine the critical concentration of chloride ions. Firstly, the chloride ion concentration was set as 0.1 mol/L, with the test results shown in Figure 3a. It could be seen that the potential continued to increase with time and reached stability after 16 h or so, indicating that the passive film was not damaged at the concentration of 0.1 mol/L. Secondly, the chloride ion concentration was set as 0.2 mol/L, with the test results shown in Figure 3b. It can be seen that the potential continued to decrease with time, indicating that the film layer was damaged at the concentration of 0.2 mol/L. The critical concentration of chloride ions should be less than or equal to 0.2 mol/L. Therefore, the critical concentration should fall within the range of 0.1 mol/L to 0.2 mol/L in the simulated pore solution.

Then, the chloride ion concentration was selected as 0.15 mol/L, with the test results shown in Figure 3c. The potential still increased with time and did not reach the critical concentration. Subsequently, the chloride ion concentration was selected as 0.16 mol/L and above, with the test results shown in Figure 3d. It was evident that the entire curve developed in three stages: in the first stage, the potential decreased sharply with time, and chloride ions passed through the passive film to reach the surface of the metal substrate; in the second stage, the potential slowly increased with time, and the passive film began to self-repair; and in the third stage, chloride ions acted on the metal substrate, peeling off the film, damaging the passive film, and decreasing the potential. Therefore, a critical concentration of 0.16 mol/L for chloride ions in the simulated pore solution at 65 °C was determined.

Afterward, electrochemical impedance spectroscopy (EIS) was used to analyze the concentrations of the four types of chloride ions mentioned above.

EIS measurement aims to obtain electrode interface structure information and analyze the damage process of passive film induced by chloride ions. The EIS measurement results could be fitted through equivalent circuits to obtain relevant electrochemical parameters and fitting curves. In equivalent circuits, the electrochemical parameters generally include R<sub>s</sub> (solution resistance), R<sub>f</sub> (film resistance), R<sub>ct</sub> (charge transfer resistance at the metal/solution interface), Q<sub>dl</sub> (double-layer capacitance at the metal/solution interface), and Q<sub>f</sub> (film capacitance). A higher transfer resistance value indicates improved film stability on the metal surface.



**Figure 3.** Potential–time curves of different concentrations of chloride ions in the depassivated simulated pore solution: (**a**) 0.1 mol/L; (**b**) 0.2 mol/L; (**c**) 0.15 mol/L; (**d**) 0.16 mol/L.

Figure 4 displays the impedance spectrum in Nyquist plots, showcasing the impact of different concentrations of chloride ions on the degradation of passive films in the simulated pore solution. The Nyquist plots under the corrosion of chloride ions with four concentrations are all double capacitive arcs. Additionally, Figure 5 illustrates the equivalent circuits. The calculated values of the corresponding electrochemical parameters are documented in Table 2. When the concentration of chloride ions was 0.1 mol/L, R<sub>ct</sub> was  $2.426 \times 10^4 \Omega$ , and R<sub>f</sub> was  $2.302 \times 10^6 \Omega$ . The passive film remained stable without leading to damage. When the concentration of chloride ions was 0.15 mol/L, the electrochemical reaction rate accelerated and the R<sub>ct</sub> decreased. Nevertheless, the critical chloride ion concentration of chloride ions increased to 0.16 mol/L, which could cause damage to the passive film, the R<sub>f</sub> decreased to  $1.364 \times 10^3 \Omega$ .

**Table 2.** Fitted electrochemical parameters through equivalent circuits about chloride ions' damage to passive film in EIS.

Concentration (mol·L <sup>-1</sup> )	R <sub>s</sub> (Ω)	R <sub>ct</sub> (Ω)	R <sub>f</sub> (Ω)	x
0.00	$8.860 \pm 0.08$	$7.334\times10^3\pm0.22$	$5.429  imes 10^{6} \pm 0.09$	$0.029\pm0.02$
0.10	$6.400\pm0.12$	$2.426  imes 10^4 \pm 0.19$	$2.302  imes 10^{6} \pm 0.12$	$0.023\pm0.03$
0.15	$10.050\pm0.23$	$3.933  imes 10^2 \pm 0.13$	${4.960} \times {10^4} \pm 0.17$	$0.005\pm0.01$
0.16	$6.150\pm0.08$	$3.601  imes 10^3 \pm 0.25$	$1.364  imes 10^{3} \pm 0.21$	$0.019\pm0.03$
0.20	$4.850\pm0.21$	$7.967  imes 10^2 \pm 0.31$	$1.834\times10^3\pm0.23$	$0.002\pm0.05$



**Figure 4.** Impedance spectrum in Nyquist plots of different concentrations of chloride ions in the depassivated simulated pore solution: (**a**) 0.00 mol/L; (**b**) 0.1 mol/L; (**c**) 0.15 mol/L; (**d**) 0.16 mol/L; (**e**) 0.2 mol/L.



Figure 5. Equivalent circuits of passive film destruction by chloride ions in simulated pore solution.

Polarization curves were used to verify the critical chloride ion concentration. Anode polarization curves for chloride ions at four concentrations are shown in Figure 6. It was evident that all four curves exhibited an absence of notable passivated zones. The lack of the passivated zone at the chloride ion concentrations below the critical threshold was due to the ability of low-concentration chloride ions to pass through the passive film and damage the substrate under the action of an external electric field. Table 3 shows that the self-corrosion current density ( $I_{corr}$ ) was 7.9433 × 10<sup>-9</sup> A/cm<sup>2</sup> at a chloride ion concentration of 0.1 mol/L. The effect demonstrated that the passive film retained a certain level of protective capability, albeit relatively minor. With the progressive increase in chloride ion concentration of chloride ions, the self-corrosion potential ( $E_{corr}$ ) shifted towards the negative direction, making corrosion more likely to occur.



**Figure 6.** Anode polarization curves—passive film destruction by chloride ions at varying concentrations in simulated pore solution.

Table 3. Polarization curve parameters—passive film destruction by chloride ions at varying concentrations.

Concentration (mol·L <sup>-1</sup> )	I <sub>corr</sub> (A·cm <sup>−2</sup> )	E <sub>corr</sub> (V)
0.10	$7.9433  imes 10^{-9}$	-0.2800
0.15	$1.0000 \times 10^{-7}$	-0.2500
0.16	$1.6596  imes 10^{-7}$	-0.3450
0.20	$1.7579  imes 10^{-7}$	-0.3563

The Mott–Schottky measurement is widely employed to investigate semiconductor properties, especially for evaluating the semiconductor properties of passive films [17,21–24]. In accordance with the band theory of solids, the film's characteristics determine its semiconductor type. When donors dominate the film, it becomes an n-type semiconductor, exhibiting an abundance of electrons in the conduction band compared to holes in the valence band. Conversely, when acceptors dominate the film, it becomes a p-type semiconductor, with more holes in the valence band than electrons in the conduction band. As per the well-known Mott–Schottky theory [25], Equation (9) is applicable to n-type semiconductors, while Equation (10) is appropriate for p-type semiconductors:

$$\frac{1}{C_{sc}^2} = \frac{2}{eN_D\varepsilon\varepsilon_0} \left[ E - E_{fb} - \frac{KT}{e} \right]$$
(9)

$$\frac{1}{C_{sc}^2} = -\frac{2}{eN_A\varepsilon\varepsilon_0} \left[ E - E_{fb} - \frac{KT}{e} \right]$$
(10)

In the given equation,  $\varepsilon$  represents the relative dielectric constant of the specimen, estimated to be approximately [26].  $\varepsilon_0$  denotes the dielectric constant of free space, which has a value of  $8.854 \times 10^{-14}$  F cm<sup>-1</sup>. *e* represents the electron charge, equal to  $1.602189 \times 10^{-19}$  C.  $N_D$  and  $N_A$  represent the donor density (cm<sup>-3</sup>) and acceptor density (cm<sup>-3</sup>), respectively.  $E_{fb}$  represents the flat band potential (*V*). *T* represents the absolute temperature (*K*), and *K* indicates the Boltzmann constant with a value of  $1.38066 \times 10^{-23}$  J·K<sup>-1</sup>.

When the NaCl concentration is 1 mol/L, significant passivation occurs, and the composition of the film layer can better reflect the characteristics, such as the characteristic product M-O-Cl. In order to accurately characterize the semiconductor performance of chloride ion damage to the passivation film, a concentration of 1 mol/L was chosen. Based on the relationship between the horizontal axis *E* and the vertical axis  $C^{-2}$ , the Mott–

Schottky curve provides valuable insights into electron conduction behavior. In Figure 7, a positive slope can be observed, indicating the presence of n-type semiconductor films in both the simulated pore solution and the solution containing 1 mol/L chloride ions. It is inferred from n-type semiconductors that the passive film primarily consists of iron oxide and iron hydrate compositions [27,28]. The formation of the passive film in n-type semiconductors is due to the doping of interstitial cations or anionic vacancies.



**Figure 7.** Mott–Schottky plots in simulated pore solution: (**a**) steady passive film; (**b**) depassivation by 1 mol/L chloride ions.

The widely recognized point defect model (PDM) is a suitable analytical tool for studying the localized corrosion behavior of metal. Extensive on-site experience and empirical evidence from experimental simulations consistently demonstrate the effectiveness of this model in elucidating the properties and structure of the passive film. Moreover, it provides a comprehensive understanding of both general and localized corrosion damage resulting from the presence of the passive film [29–33]. A dynamic equilibrium exists between the formation of the passive film at the metal substrate/film interface and its dissolution at the film/solution interface. According to the PDM model, when the solution contains chloride ions, chloride ions form a hydrate with water in the solution ( $Cl^- \cdot nH_2O$ ). At the film/solution interface, the presence of oxygen vacancies ( $V_0''$ ) leads to the adsorption of the hydrate, which subsequently reacts with it through Mott–Schottky pair formation. This process generates pairs of oxygen vacancy/metal ion vacancy ( $V_M'$ ). Reaction (11) can be used to show that this process produces a p-oxygen/metal ion vacancy as follows:

$$V_o'' + Cl^{-} \bullet nH_2O \leftrightarrow Cl_o^{-} + nH_2O \xrightarrow{Mott-Schottky \ pair} V_M^{\chi'} + \frac{\chi}{2} V_o'' \tag{11}$$

The presence of oxygen vacancies promotes the adsorption of chloride ion hydrates, leading to the generation of additional metal ion vacancies. These excess metal ion vacancies accumulate at the metal substrate/film interface, causing the separation of the passive film from the substrate. As a result, the growth of the passive film is hindered, and the original dynamic equilibrium is disrupted. Consequently, the passive film solely undergoes dissolution, ultimately resulting in destruction. Hence, an increased presence of oxygen and metal ion vacancies within the passive film corresponds to a higher concentration of donors or acceptors. Consequently, the passive film becomes more vulnerable to damage. Equation (9) provides a means of calculating the donor density ( $N_D$ ) and flat band potential ( $E_{fb}$ ), with results listed in Table 4. The donor density and flat band potential increased, and the corrosion resistance of the passive film decreased with 1 mol/L chloride ions added to the simulated pore solution.

Solution	State	$N_D$ (cm <sup>-3</sup> )	E <sub>fb</sub> (V)	Туре
Simulated pore solution	passivated	$2.9051 \times 10^{21}$	0.4860	n
Simulated pore solution with 1 mol/L chloride ions	depassivated	$1.9796 \times 10^{22}$	0.7287	n

Table 4. Electrochemical parameters calculated from the Mott-Schottky plots.

As the donor density of the passivated film gradually increases, the probability of damage or pitting corrosion of the oxide film increases. As the flat band potential of the passivated film decreases, its corrosion resistance increases.

## 3.3. Analysis of the Film Components

The components of the film can be obtained using XPS measurement. XPS spectra of the passive film in the simulated pore solution are shown in Figure 8. Two peaks (Fe 2p3/2) of Fe 2p in the spectrum were Fe (OH)<sub>2</sub> (Fe<sup>2+</sup>) and FeOOH (or Fe<sub>2</sub>O<sub>3</sub>), with binding energy of 709.7 eV and 711.45 eV, respectively. Four peaks of O 1s spectrum were Fe<sub>2</sub>O<sub>3</sub>, FeOOH, Fe(OH)<sub>2</sub> (OH<sup>-</sup>), and H<sub>2</sub>O, with binding energy of 529.5 eV, 529.9 eV, 531.3 eV, and 532.9 eV, respectively. Therefore, the passive film in the simulated pore solution consisted of Fe(OH)<sub>2</sub>, FeOOH, and Fe<sub>2</sub>O<sub>3</sub> compositions.



Figure 8. XPS spectra of the passive film in simulated pore solution.

The passive film subjected to the destruction of 1 mol/L chloride ions (Cl<sup>-</sup>) was analyzed by XPS, as shown in Figure 9. The characteristic peaks (2p1) of Cl were 199.1 eV and 200.5 eV, the Cl<sup>-</sup> on the surface had the binding energy of 199.1 eV, and another peak was that of M-O-Cl. Concentration gradient generation will promote the diffusion of Cl<sup>-</sup> toward the inner of the passive film when Cl<sup>-</sup> exists on the passive film surface [34]. O had three characteristic peaks (1s), Fe<sub>2</sub>O<sub>3</sub> had the binding energy of 529.4 eV, 531.3 eV corresponded to OH<sup>-</sup>, and H<sub>2</sub>O left on the surface of the film had the binding energy of 535.8 eV. Fe had two characteristic peaks (2p3/2). That at 707 eV was a track of the iron matrix, and another peak was the overlap of the peaks of Fe<sup>2+</sup> and Fe<sup>3+</sup>, with the binding energy of about 710.3 eV~710.4 eV. Thus, the composition of the film was M-O-Cl, Fe<sub>2</sub>O<sub>3</sub>, and Fe(OH)<sub>2</sub>.



Figure 9. XPS spectra of the damaged passive film by 1 mol/L chloride ions in simulated pore solution.

## 3.4. Surface Morphology of Passive Film

Figure 10 shows SEM images of steel in different chloride ion concentrations. It can be seen from Figure 10a–c that steel does not corrode after passivation at chloride ion concentrations below 0.15 mol/L, but pitting occurs when the concentration rises to 0.16 mol/L (Figure 10d). The critical concentration of 0.16 mol/L chloride ion can be considered. Because 0.2 mol /L chloride ion concentration is greater than the critical concentration, the passivation film on the casing surface can be effectively destroyed, and the morphology of the passivation film on the casing surface after damage can be observed. Figure 10e shows that pitting often occurs on metal with passivated film surfaces. When a certain point of the steel is damaged, the matrix of the damaged and undamaged areas forms a metastable corrosion battery. The passivation surface is the cathode, and has an area much larger than the activation area. Corrosion develops more deeply, forming corrosion pits.



**Figure 10.** SEM diagram of steel corroded at different chloride ion concentrations, (**a**) 0.00 mol/L; (**b**) 0.10 mol/L; (**c**) 0.15 mol/L; (**d**) 0.16 mol/L; (**e**) 0.20 mol/L.

## 4. Conclusions

- 1. Here, we propose a method to determine the critical concentration of chloride ions for the destruction of the passive film. The critical chloride ion concentration can be determined using a potential-time curve, anode polarization curve, and electrochemical impedance spectroscopy testing.
- 2. The critical concentration of chloride ions for the destruction of the passive film in a simulated pore solution was determined to be 0.16 mol/L at a temperature of 65 °C and a pH value of 12.5.
- 3. The passive film subjected to chloride ion damage was the n-type semiconductor, just like the steady-state passive film in equilibrium. The passive film contained more oxygen vacancies and metal ion vacancies. In the passive film, an increase in the concentration of donors or acceptors made the film more susceptible to damage.
- 4. The components of the passive film eroded by chloride ions were M-O-Cl, Fe<sub>2</sub>O<sub>3</sub>, and Fe(OH)<sub>2</sub>. Compared with the steady-state passive film, the characteristic product was M-O-Cl.
- 5. Under the five chloride ion concentrations used in the experiment, only 0.16 mol/L and 0.20 mol/L chloride ion conditions resulted in pitting corrosion on the surface of

P110 casing steel, which could correspond to the conclusions obtained from electrochemical experiments.

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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author. The data are not publicly available the involvement of some private data.

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