



# Article A Study of the Mechanisms and Kinetics of the Localized Corrosion Aggravation of Ductile Iron in a Harsh Water Quality Environment

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Abstract: Ductile iron is a high-strength cast iron material. The spherical graphite obtained by inoculation treatment effectively improves the mechanical properties of cast iron, resulting in higher strength than carbon steel. However, severe corrosion may occur under specific circumstances, especially in thermal water pipelines. In this paper, the corrosion mechanisms at the main defective points of ductile iron were investigated using microscopic morphological characterization after accelerated tests combined with numerical simulations. The influence law of each environmental factor on the corrosion kinetics of ductile iron in a complex water quality environment was studied using dynamic potential polarization tests. The results showed that the main causative factors leading to the increased corrosion of ductile iron were the presence of tail-like gaps on its surface, and the crescent-shaped shrinkage and loosening organization around the graphite spheres. After mechanical treatment was applied to eliminate the obvious defects, the number of corrosion pits was reduced by 41.6%, and the depth of the pits was slowed down by 40% after five days. By comparison, after ten days, the number of pits was reduced by 51%, and the depth of the pits was slowed down by 50%. The dynamic potential polarization test results show that the dissolved oxygen concentration has the greatest influence on the corrosion of ductile iron in the simulated water environment; meanwhile, the water hardness can slow down the corrosion of ductile iron. The relative influence of each environmental factor is as follows: dissolved oxygen concentration > temperature > immersion time > water hardness >  $pH > Cl^{-}$ .

Keywords: ductile iron; harsh water; mechanical treatment; localized corrosion

# 1. Introduction

With increasing demand for water resources, the laying of water transmission pipelines has been gradually accelerated [1]. Additionally, the demand for water transmission pipelines such as steel pipes, ductile iron pipes, pre-stressed steel cylinder concrete pipes (PCCP), and sandwich glass steel pipes has increased sharply. In the application of cast pipes with cement lining, harmful ions such as  $Cr^{6+}$  often enter into the water from contaminated cement and endanger human health. With the increased use of cement-free lined cast iron pipes in plumbing lines, the fluid in the pipeline comes into direct contact with the line material. In these circumstances, the flow rate and shear stress destroy the resulting corrosion film on the material's surface [2], and elevate the potential risk of the corrosion-based deterioration of pipelines [2–8]. This may endanger the safe operation



Citation: Wang, B.; Liu, T.; Tao, K.; Zhu, L.; Liu, C.; Yong, X.; Cheng, X. A Study of the Mechanisms and Kinetics of the Localized Corrosion Aggravation of Ductile Iron in a Harsh Water Quality Environment. *Metals* **2022**, *1*2, 2103. https://doi.org/10.3390/ met12122103

Academic Editor: Renato Altobelli Antunes

Received: 31 October 2022 Accepted: 5 December 2022 Published: 7 December 2022

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**Copyright:** © 2022 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/). of the entire water supply system and lead to a series of problems, such as water quality deterioration, and ecological and economic losses.

In non-cement-lined water supply pipelines, the water temperature, pH [1,9], oxygen content, and chloride ion concentration are important factors that lead to the immersion corrosion of the transmission pipeline; these factors exist in addition to the flow immersion corrosion effect. Stefano [3] described the effect of scaling ions (Ca<sup>2+</sup> and Mg<sup>2+</sup>) in water quality on the corrosion process of geothermal galvanized steel pipes. The concentration of Zn<sup>2+</sup> and OH<sup>-</sup> has a clear effect on the formation of the nuclei of corrosion products in a solution with a higher concentration of scaling ions, which results in the presence of spherical corrosion products and scales on the surface of the pipe. This corrosion product mainly comprises zinc oxide, calcium carbonate, and magnesium carbonate, which could decrease the corrosion rate. Georgii [6] showed the effect of different flow rates on the corrosion process of mild steel, whereby, at higher flow rates (0.19–0.45 m/s), the protective properties of the metal surface layer were brought about by enhanced mass transport. In this condition, crystals of calcite and iron oxide could be formed in the cathodic and anodic regions, respectively, leading to the formation of a self-healing barrier film that blocked the oxygen supply and prevented the release of iron into the water.

Ductile iron, as the material most widely used in aqueducts, can lead to the accelerated damage of aqueducts due to microstructural defects such as microscopic shrinkage loosening on the material's surface, which can increase the corrosion area of castings. These defects are also more likely to cause the formation of pits. However, these defects could be improved by suitable surface mechanical treatment techniques [10,11], thus enhancing the corrosion resistance of ductile iron castings in aqueduct services.

Studies of the corrosion resistance of ductile iron are currently dominated by single influencing factors [12–16]. The corrosion of ductile iron [14] under cyclic salt spray exposure consists of three processes: (i) the pitting of ferrite, (ii) the inward oxidation of the austenitic ferrite matrix, associated with the formation of a dense inner layer, and (iii) the mixed oxidation of the matrix, associated with the formation of a rust layer on the sample surface, where chloride ions are transferred and become involved in the corrosion reaction by changing the properties and composition of the rust layer. The levels of corrosion resistance of carbon steel and ductile iron castings show significant differences at different levels of chloride ion content [15]. An increase in the chloride content leads to an increase in the corrosion rate, and carbon steel is more susceptible to damage from chloride than ductile iron castings in a multi-factor coupled environment remain unclear.

This study investigated the influence of surface cracks on the corrosion resistance of ductile iron castings. In this work, the main causative factors for the acceleration of the corrosion of ductile iron materials were investigated, and a variety of water quality environments that may exist in water pipelines were simulated. We offer a quantitative ranking of the degree of influence of each environmental factor on the corrosion kinetics of ductile iron, and screen out the environmental factors that have the greatest influence on the acceleration of the corrosion of ductile iron at each corrosive stage. The main environmental factors that influence the corrosion resistance of ductile iron castings were identified.

# 2. Materials and Methods

# 2.1. Materials

The chemical composition of the ductile iron castings used in this work is 3.75% C, 1.8% Si, 0.45% Mn, 0.07% P, 0.012% S, 0.06% Mg, and Bal. Fe. Defects including shrinkage and holes can be easily formed on the material's surface in the manufacturing process. Two different specimens were produced for this research. One type of specimen was produced by being slightly mechanically ground to 2000#, with surface defects maintained on the specimen surface. Another type of specimen was mechanically ground to 2000# until the defect layer disappeared. All of the specimens were polished to a mirror finish with diamond abrasives with a particle size of  $1.0 \mu$ m.

## 2.2. Environmentally Simulated Solution

Before the immersion experiment, nitrogen was introduced into the environment; this required deoxygenation to simulate an anoxic environment, in which the simulated liquid was deoxygenated at a constant speed of every 250 mL for 3 h. The concentration was then measured and controlled at  $0.3 \text{ mg} \times \text{L}^{-1}$ , and then start the immersion experiment. A total of 8 different environments were configured for the experiments, as shown in Table 1. The water hardness was adjusted with CaCO<sub>3</sub>, and the Cl<sup>-</sup> concentration was adjusted with NaCl. The same batch was immersed in a large 8-hole water bath during the immersion process. A small water bath was used for the electrochemical measurements to ensure a constant temperature during the test.

No.	1	2	3	4	5	6	7	8
Hardness/ppm	20	20	20	20	80	80	80	80
pH	7	7	10	10	7	7	10	10
Temperature/°C	60	90	90	60	90	60	60	90
Čl <sup>-</sup> /ppm	20	120	20	120	20	120	20	120
Oxygen concentration/mg*L <sup>-1</sup>	0.3	0.3	6.5	6.5	6.5	0.3	6.5	0.3

Table 1. Characteristic parameters of the simulated solution.

# 2.3. Autoclave Immersion Experiment

Solution environment no. 8 was selected for the experiment. Ductile iron samples of 50 mm  $\times$  25 mm  $\times$  4 mm, both with and without surface mechanical treatment, were polished with silicon carbide paper (2000#) and then cleaned with ethanol and dried using cold air. After determining the original weight of the specimen, the specimen was suspended from the inner wall of the beaker using a nylon fishing line. During the immersion process, the autoclave was pressurized to 1 MPa and the water temperature was controlled at 90 °C; the test cycles were 1220 h and 2440 h. Four parallel specimens were prepared for each material, and three of them were used to determine the loss in thickness. The last sample was used for scanning electron microscopy (SEM) and laser scanning confocal microscopy (CLSM) characterization. The rust on the specimen was ultrasonically cleaned in a descaling solution that consisted of 98%HCl (500 mL), H<sub>2</sub>O (500 mL), and hexamethylenetetramine.

# 2.4. Electrochemical Test

Electrochemical measurements were performed using the PARSTAT4000A electrochemical workstation and electrochemical system using the classic three-electrode system with a platinum sheet as the counter electrode, a saturated calomel electrode (SSCE) as the reference electrode, and ductile iron samples as the working electrodes. Electrochemical samples were sealed with high-temperature-resistant epoxy resin. The exposure area was 1 cm<sup>2</sup>. The open circuit potential (OCP) was measured for at least 30 min until a steady state was reached; then, electrochemical experiments were conducted. Three sets of parallel experiments were set up for each environment to minimize experimental errors [17].

Potentiodynamic polarization curves were obtained by performing kinetic polarization curve measurements with a scan rate of 0.333 mV/s and a scan potential range of -0.5 V/OCP to 0.8 V/OCP.

The test conditions for electrochemical impedance spectroscopy (EIS) in each solution were the same as the working electrode used for the kinetic potential polarization test. The frequency range for EIS was from 100 kHz to 10 mHz with an amplitude of 5 mV (rms) at the open circuit potential.

#### 2.5. Simulation Model Calculations

The model uses the same solution environment as the autoclave immersion experiment. Finite element simulation was performed using Comsol software [18–21]. Irrespective of insoluble substances, the modeled electrolyte species are  $H^+$ ,  $OH^-$ ,  $Cl^-$ ,  $Na^+$ , and

Fe<sup>2+</sup>. Fixed concentrations and electrolyte phase potential were set at the top horizontal electrolyte boundary, facing the air. The iron dissolves at the electrode surface:

$$\operatorname{Fe}^{2+} + 2e^{-} \Leftrightarrow \operatorname{Fe}(s)$$
 (1)

Additionally, the kinetics depend on pH ( $i_0$  proportional to H<sup>+</sup>):

$$i_{loc} = i_0(\exp(\frac{\partial_a F\eta}{RT}) - \exp(-\frac{\partial_c F\eta}{RT}))$$
(2)

$$i_{loc} = i_0 (c_R \exp(\frac{\alpha_a F \eta_{ref}}{RT}) - c_0 \exp(-\frac{-\alpha_c F \eta_{ref}}{RT}))$$
(3)

Equation (2) is a Butler–Volmer expression [22], where  $\alpha_c$  denotes the cathodic charge transfer coefficient,  $\alpha_a$  is the anodic charge transfer coefficient, and  $i_0$  is the exchange current density. The kinetic equation is then coupled with the solution environment. Equation (3) is a Butler–Volmer expression with concentration dependence. This type of expression allows for more freedom in defining the concentration-dependent Butler–Volmer type of expressions, where the anodic and cathodic terms of the current density expression typically depend on the local concentrations of the electroactive species at the electrode's surface.  $c_R$  and  $c_0$  are dimensionless expressions, describing the dependence on the reduced and oxidized species in the reaction.

 $\eta$  is the overpotential given by

$$\eta = E_{\rm m} - E_{\rm eq} \tag{4}$$

 $E_{\rm m}$  is the electrode potential and  $E_{\rm eq}$  is the equilibrium potential. The metal potential is set to a fixed value, resulting in a mixed potential not affected by the local pit corrosion. Ions such as Cl<sup>-</sup> may also be transported in order to maintain electroneutrality. The transport of ions, in combination with the pit shape, determine the local pH. If the iron oxidation reaction is catalyzed by H<sup>+</sup>, a lower pH within the pit results in faster metal dissolution compared to the metal surface outside the pit. The tertiary current distribution and Nernst–Planck interface defines the mass and ion transport. The water-based charge balance model with electroneutrality defines the H<sup>+</sup> concentration and the OH<sup>-</sup> concentration as built-in variables, and automatically defines the water autoprotolysis equilibrium. The separator node is used to define the pit as a porous structure. Deformed geometry handles the deformation of the pit. The multiphysics nodes couple the electrochemistry to the deformation.

#### 3. Results and Discussion

# 3.1. Exploration of the Corrosion Mechanisms of Ductile Iron Shrinkage Holes

# 3.1.1. Microstructure Characteristics

As shown in Figure 1a–f, a large number of shrinkage holes, which are visible to the naked eye, can be seen on the surface of the ductile iron pipe that did not receive surface mechanical treatment. Additionally, these holes are deep and cover a wide area. These holes are highly likely to become areas of aggressive ion accumulation in a harsh environment. This would accelerate the formation of a local acidified environment, in which the dissolution of the iron matrix would be promoted. After the surface mechanical treatment, these obvious defects on the surface of the ductile iron pipe are removed; the microscopic morphology is shown in Figure 1g–k. It can be seen that the shrinkage holes on the surface of this specimen are significantly reduced. The surface uniformity of this specimen is better, and the graphite balls are uniformly distributed on the surface.

# 3.1.2. Corrosion Morphology

To investigate the corrosion process of the ductile iron pipe in the real service environment of thermal pipeline, an immersion corrosion test was conducted in the autoclave. The corrosion morphology of the two different specimens after different periods of immersion is shown in Figure 2. As the immersion time increases, there was a marked increase in the corrosion product (Figure 2a,b,e,f). As shown in Figure 2c,d, the surface of the ductile iron without surface mechanical treatment featured large pits after the rust removal, indicating that serious localized corrosion was initiated on the specimen's surface. As the acceleration time increases, the number of large-sized holes increases, and local corrosion intensifies [23,24]. The whole interface between the graphite spheres and the matrix was dissolved on the ductile iron specimen that had not received surface mechanical treatment. This is primarily the result of the holes and shrinkages formed around the graphite spheres. Aggressive ions such as Cl<sup>-</sup> would be preferentially enriched at these defect sites, resulting in the local acidification of the solution environment. The interface with high electrochemical activity would be dissolved easily. The mechanically treated ductile iron sample shows slight corrosion morphology (Figure 2g). Serval shallow pits were randomly distributed on the specimen's surface after 120 h of immersion. The corrosion is relatively mild, mainly comprising the pits left by the dislodging of graphite balls after the spread of corrosion. As the immersion time increased to 240 h, larger sized pits could be seen on the surface of the mechanically treated ductile iron specimen (Figure 2h). This is mainly due to the integration of the pits formed after the dislodging of the graphite balls. However, the number of pits was significantly smaller than that of the ductile iron samples that had not received surface mechanical treatment (Figure 2d). As the upper graphite sphere is detached, the graphite sphere buried at the bottom is also exposed.



**Figure 1.** The microscopic morphology of the two ductile iron samples before the experiment. (**a**–**f**) ductile iron pipe with no surface mechanical treatment, (**g**–**k**) ductile iron pipe with surface mechanical treatment.



**Figure 2.** Surface corrosion morphology of different specimens after the immersion test. (**a**,**b**,**e**,**f**) Before and (**c**,**d**,**g**,**h**) after the corrosion rust removal. (**a**,**c**,**e**,**g**) Immersion at 120 h, and (**b**,**d**,**f**,**h**) immersion at 240 h. (**a**–**d**) Ductile iron with no surface mechanical treatment, (**e**–**h**) Ductile iron with surface mechanical treatment.

The SEM observation results show that there are many shrinkage holes and tail-like crevices on the surface of the ductile iron. After mechanical polishing to remove these obvious defects and applying a high-pressure immersion corrosion test, the degree of corrosion on the specimen's surface is significantly reduced, as is the number of local corrosion holes. It can initially be concluded that the corrosion resistance of ductile iron is significantly improved by the use of suitable surface mechanical treatments.

In order to analyze the development of the different pits in a quantitative manner, the 3D corrosion pit morphology of the specimen after rust removal was observed using confocal laser scanning microscopy (CLSM). The results are shown in Figure 3. Due to the presence of more tail-like defects with the shrinkage and loosening of the tissue, the corrosion on the surface of the non-mechanically treated ductile iron samples increased after the immersion test (Figure 3a,c). There was also an increase in the depth of the localized corrosion pits and an increase in the corrosion area. In contrast, the surface-treated ductile iron samples corroded slightly (Figure 3b,d); this is consistent with the results observed using SEM.

The pits on the surfaces of both samples were analyzed quantitatively and the results are shown in Figures 4 and 5. After 120 h of immersion corrosion, the number of pits  $(124/15 \ \mu m)$  and the maximum depth of the pits in the surface of the mechanically treated ductile iron samples were significantly lower than in the untreated specimens  $(220/25 \ \mu m)$ . Equations (5) and (6) are used to describe the effect of the surface treatment on improving the pitting resistance of the ductile iron material:

$$pren(number) = \frac{n - n_{st}}{n} \times 100\%$$
(5)

$$pren(depth) = \frac{d - d_{st}}{d} \times 100\%$$
(6)

where *n* is the number of etch pits on the ductile iron without surface treatment, and  $n_{st}$  is the number of etch pits for the ductile iron with surface treatment. Additionally, *d* is the maximum pit depth for the ductile iron without surface treatment, and  $d_{st}$  is the maximum pit depth for the ductile iron with surface treatment. The results show that the number

of pits decreased by 43.6%, and the maximum pit depth reduction rate reached 40%. The K-value distribution results show that, after the 120 h immersion corrosion test, the volume of etch pits on the surface of the ductile iron samples without surface mechanical treatment reached  $2500-10,000 \ \mu m^3$ . The K value distribution is not completely concentrated in the small corrosion pit area; it is evenly distributed between the medium and large corrosion pits. This indicates that the large pits observed by SEM are not coincidental. As shown in Figure 4b, the volume of corrosion pits on the surface of the sample is distributed below  $2500 \ \mu m^3$  after the surface mechanical treatment.



Figure 3. 3D corrosion morphology of different specimens after the immersion test. (a,c) represent the ductile iron that had not received surface mechanical treatment; (b,d) represent the ductile iron that had received surface mechanical treatment.



**Figure 4.** The number of etching pits and the K-value statistics of the CLSM results after the 120 h accelerated test. (**a**,**b**) Ductile iron with no surface mechanical treatment, (**c**,**d**) ductile iron with surface mechanical treatment.



**Figure 5.** Distribution of the number of etch holes as a function of their size and the statistics of the K value of the CLSM results after the 240 h accelerated test. (**a**,**b**) Ductile iron with no surface mechanical treatment, (**c**,**d**) ductile iron with surface mechanical treatment.

After continuing the immersion in the autoclave up to 240 h, the corrosion of both ductile iron samples increased to different degrees. Specifically, the number, volume, and depth of pits increased, especially for specimens that had not received surface mechanical treatment. Although the surface corrosion pits on the surface of the mechanically treated ductile iron samples remained small, medium and large volume corrosion pits with volumes greater than 2500  $\mu$ m<sup>3</sup> began to appear, and reached a maximum volume of 8000  $\mu$ m<sup>3</sup>. These occasional large pits are formed by the fusion of several small pits during the corrosion pits with a volume distribution of 2500 to 10,000  $\mu$ m<sup>3</sup> was, predictably, increased for the samples without surface mechanical treatment. Calculations show that, in the surface-treated ductile iron material, the number of corrosion pits can be reduced by 51% and the maximum pit depth is slowed by 50% after 240 h of immersion.

# 3.1.3. Mechanisms of the Localized Corrosion Initiation

The CLSM results showed that the corrosion of the ductile iron was effectively slowed down after the mechanical treatment was used to eliminate the obvious defects on the surface of the ductile iron. Combined with the SEM observations, these finding suggest that the main reason that the increased corrosion of the ductile iron occurs in the simulated water quality is due to localized corrosion [23,25,26]. After the ductile iron that had not had its surface defects removed was soaked in the autoclave, there were many large corrosion pits on the surface of the sample. These local corrosion pits are large, deep, and numerous. Additionally, when these surface defects are removed, the surface of the ductile iron is basically flat, except for a very small number of small holes. However, as the corrosion proceeds, the surface will continue to exhibit shrinkage holes and defects, and the rate of corrosion will gradually increase.

Observation results by SEM, the localized corrosion process can be described as follows: (1) With the aggressive ions accumulated in the defects at the matrix and the graphite nodule, the initiation of localized corrosion is triggered (Figure 6a). (2) With the evolution of the

localized corrosion, the galvanic effect [27–29] between the matrix and graphite promotes the development of localized corrosion (Figure 6b). (3) With the growth of smaller pits, larger pits would be formed, resulting from the consolidation of these smaller pits (Figure 6c). The depth of the pits increases as the small graphite spheres continue to fall off during the corrosion process.



Figure 6. The localized corrosion initiation process in ductile iron (a-c).

3.1.4. Simulation of the Corrosion Process

In order to further confirm the conclusion offered in 3.1.3, and to describe clearly the dynamic process of the increased corrosion of ductile iron by shrinkage holes, a finite element simulation [30–33] was used to assess the ductile iron's surface at the shrinkage gap. The model defines the kinetic characteristics of the actual electrolyte environment and the cast iron substrate. The planar geometry and mesh division of the model are shown in Figure 7. The whole model consists of spherical graphite, an electrolyte, and a cast iron electrode. Marking points 1,2,3 facilitates the observation of shape changes due to corrosion in the later simulation studies.



Figure 7. Schematic diagram of the geometry and meshing of the simulation model.

In the early stages of corrosion, when uniform electrochemical corrosion occurs over the entire area, the crescent-shaped gaps around the graphite were filled with the electrolyte solution (Figure 7b). This is because the shape of the gap was not extended when corrosion occurred for 1d (Figure 8a,e). When corrosion occurs for 3 d (Figure 8b,f), the shape of the gap changes due to corrosion. Additionally, because of charge conservation, as Fe<sup>2+</sup> dissolves and oxygen are consumed, higher amounts of H<sup>+</sup> and Cl<sup>-</sup> in the solution diffuse into the gap. The pH and Cl<sup>-</sup> concentrations also changed. The highest Cl<sup>-</sup> concentration was found at the bottom of the gap (point 3), reaching 190 ppm, and the pH decreased to 9. This also resulted in a concentration difference within the gap from the overall solution environment [25,34].The gap kept expanding. After 7 d of corrosion (Figure 8c,g), the gap gradually evolved into a teardrop-shaped etch pit [35]. The Cl<sup>-</sup> concentration in the gap reached a maximum of 260 ppm and the pH dropped to a minimum of 8.9. At this point, the gap expanded at an increasingly rapid rate. This continuous anodic dissolution also continuously produced  $Fe^{2+}$  and consumed oxygen, prompting more migration of Cl ions and transport of H into the crescentic gap. further acidifying the solution in the interstitial space. Because of this vicious cycle, the initial gap gradually expanded into a teardrop-shaped corrosion pit at 10 d (Figure 8d,h). This is consistent with the statistics provided by the CLSM. The pH of the corrosion pits (point 3) was only 8.32 at this time, and the Cl<sup>-</sup> concentration increased to 700 ppm.



**Figure 8.** The pH and Cl<sup>-</sup> diffusion at different times. (**a**–**d**) culated results of pH at 24 h, 72 h, 168 h, and 240 h, (**e**–**h**) alculated results of Cl<sup>-</sup> diffusion at 24 h, 72 h, 168 h, and 240 h. On this scale, 1 represents 100 ppm concentration.

According to the guidelines of the physical model adopted in this work, as corrosion occurs, the variation in the anode's surface potential in the crescent-shaped gap is shown in Figure 9a~d. Inside the gap, the local potential difference in the interface iron/near solution gradually becomes more negative from the top to the bottom of the gap. The electrode potential at the top of the gap (point 1) was -0.62 V at 10 h and 90 h. The anode's metal corrosion potential at the bottom of the slit (point 3) decreased to -0.65 V. A more negative electrode surface potential also leads to a higher corrosion rate and more severe corrosion at the bottom of the crevice (Figure 9c). This is because, with the negative shift of the electrode and the electrolyte (Equation 4), which results in an enhanced corrosion kinetic process. At 240 h, the surface corrosion potential of the electrodes inside the gap continues to shift negatively. The potential at point 1 decreases to -0.65 V and the surface potential at point 3 decreases to -0.73 V. The corrosion process still gradually increases.

# 3.2. *The Effect of the Water Environment on the Corrosion Kinetics of Ductile Iron* 3.2.1. Corrosion Rate Analysis

Figure 10 shows the corrosion rate of the two ductile iron materials after the autoclave immersion experiment. After 120 h of immersion, the corrosion rate of the ductile iron samples without surface treatment was much higher than that of the surface-treated samples. With the immersion time increased to 240 h, the corrosion rate of the surface-treated samples was still lower than the specimen without surface treatment. This corrosion kinetic law indicates that the corrosion rate of ductile iron can be substantially slowed down after surface treatment to eliminate obvious defects on the surface. It also shows that the corrosion damage of ductile iron in a harsh water quality environment is caused by very severe local corrosion [36,37] due to the formation of dense differential cells [38] by shrinkage holes.



**Figure 9.** Calculated relative changes of local metal potential at different times. (**a**–**c**) potential distribution clouds at 10 h, 90 h, and 240 h, respectively, (**d**) relative changes of local potential of the metal surface along the y-direction, and (**e**) the corrosion rate distribution along the y-direction.



Figure 10. Corrosion rates of different ductile iron samples after different periods of immersion.

# 3.2.2. Electrochemical Test

The polarization curve can accurately reflect the corrosion kinetics of the electrode. It is able to express both the cathodic oxygen consumption and the anodic electrode dissolution. It is widely used in metal corrosion studies [23,39–42]. The results are shown in Figure 11. The figure shows that the two ductile iron samples exhibit the same electrochemical reaction mechanism in different solution environments. The cathodic process primarily concerns the consumption of oxygen, and the anodic process concerns the dissolution of the metal. Under low oxygen dissolution conditions, the cathodic process is limited. It is worth noting that the surface-treated ductile iron samples in solution no. 4 are always passivated after a certain anodic potential polarization. The two materials also exhibit significant differences in their corrosion kinetics at different immersion cycles when the water environment changes.





**Figure 11.** Dynamic potential polarization curves of two types of ductile iron during different periods of immersion in eight simulated water conditions, (**a**–**c**) are ductile iron without mechanical treatment; (**d**–**f**) are ductile iron with mechanical treatment.

The polarization curve data in the range of  $\pm$ (100 to 125) mV, relative to the open circuit potential, were intercepted to fit the i<sub>corr</sub>, and the results of the fit are shown in Table 2. At 0 d, the i<sub>corr</sub> of the unsurfaced samples was higher than that of the surface-treated samples in all simulated environments (Figure 12a). However, the i<sub>corr</sub> of the surface-treated samples started to improve as the immersion time increased. By 10 d of immersion, the i<sub>corr</sub> of the surface-treated samples in the No. 3, 5, 7, and 8 solutions had surpassed that of the unsurfaced samples (Figure 12c). This verifies the hypothesis previously made in the autoclave immersion experiment. The mechanical treatment eliminates the obvious defects on the ductile iron surface; however, as the corrosion proceeds, uniform corrosion will cause defects to gradually be exposed on the sample surface, accelerating the occurrence of local corrosion. Overall, compared to the i<sub>corr</sub> average, the surface-treated ductile iron strand to the non-surface-treated samples.

To confirm the findings of the kinetic potential test, an electrochemical workstation was used to perform EIS tests on both materials under the same conditions in solutions no. 2, 4, 5, and 8. The nyquist plot (Figure 13a) shows that the EIS in solutions no. 8 and 7 appears to be characterized by high frequency capacitive arcs and low frequency Warburg impedance. It shows that there is a diffusion impedance for the electrochemical reaction under this condition. The equivalent circuit in Figure 13h was used to fit the EIS data. Additionally, only one capacitive arc exists for the EIS in solutions no. 3 and 5. The equivalent circuit in Figure 13g was used to fit the EIS data [43]. R1 is the solution resistance, and R2 is the equivalent resistance of the charge transfer impedance in the interface region. CPE1 is the equivalent capacitance of the bilayer in the interface region, and W1 is the Warburg impedance [44,45].

Times(d)	i <sub>corr</sub> without Mechanical Treatment(A/cm <sup>2</sup> )								
	1	2	3	4	5	6	7	8	
0	8.3	16.8	8.7	15.6	15.4	14.8	17.4	4.6	
3	6.8	5.9	5.1	6.7	5.0	9.6	11.1	6.3	
10	6.9	7.6	9.7	9.2	5.2	9.1	4.2	3.1	
Average	7.3	10.1	7.8	10.5	8.5	11.1	10.9	4.6	
			i <sub>corr</sub> v	with mechanica	al treatment(A	/cm <sup>2</sup> )			
	1	2	3	4	5	6	7	8	
0	6.2	2.9	7.2	0.2	13.3	11.8	7.7	2.6	
3	3.9	5.8	6.2	0.6	4.2	10.8	4.8	4.2	
10	5.9	4.7	10.2	2.1	6.7	3.6	19.2	4.5	
Average	5.3	4.5	7.9	1.0	8.1	8.7	10.6	3.8	

Table 2. Fitting results of icorr by potentiodynamic linear polarization scanning.



Figure 12. Fitting results of the i<sub>corr</sub> values of different ductile iron samples (a–c).



**Figure 13.** EIS test results. (**a**–**c**) are nyquist plots, (**d**–**f**) are bode plots and phase angles, (**g**,**h**) are the equivalent circuits, (**i**,**j**) are the comparison fitting results of  $R_P$  at 0 d and 10 d.

The fitted results are shown in Table 3. It can be seen, the charge transfer resistance of the surface-treated ductile iron samples is generally higher at the beginning of the immersion process (Figure 13i). As the immersion time increases, the Rp of the surface-treated ductile iron material starts to decrease at 10 d of corrosion. A weaker corrosion inhibition effect was exhibited. This also explains the sudden increase in the i<sub>corr</sub> of the surface-treated ductile iron at 10 d (Figure 12c).

Times(d)	$R_s$ without Mechanical Treatment ( $\Omega/cm^2$ )				$R_p/W_R$	$R_p/W_R$ without Mechanical Treatment ( $\Omega/cm^2$ )				
	3	8	5	7	3	8	5	7		
0	112	58	327	31	2848	526/ 3	967	100 /2		
3	84	69	226	46.	989	139.4/0.5	821	163 /4		
10	49	108	187	45	3149	193/	1020	445 /0.2		
Times(d)	$R_s$ with mechanical treatment ( $\Omega/cm^2$ )				R <sub>p</sub> /W	$R_p/W_R$ with mechanical treatment ( $\Omega/cm^2$ )				
	3	8	5	7	3	8	5	7		
0	102	83	297	52	6222	4785	1493	171/ 36		
3	118	91	154	35	1409	366.1 /62	547	182 /14		
10	58	109	133	47	58.26	150/1.1	650	220 /4.7		

**Table 3.** Fitting results of  $R_s$ ,  $R_p$ , and  $W_R$  by EIS.

#### 3.2.3. The Influence of Environmental Factors

In order to further quantify the influence of different water quality environmental factors on the corrosion process of ductile iron with different treatments, the xgboost algorithm was used to compare the influence of environmental factors (pH, Cl<sup>-</sup> concentration, hardness, oxygen content, and temperature) on the corrosion ductile iron with different surface states. The calculation results are shown in Figure 14.

As can be seen from Figure 14a, for the ductile iron material without surface mechanical treatment, the presence of dissolved oxygen in the solution plays a major controlling role among all environmental factors, contributing to 68.5% of the increase in i<sub>corr</sub>. The remaining environmental factors were evenly distributed below 15% in terms of the degree of influence on  $i_{corr}$  [46,47]. It is noteworthy that the contribution of Cl<sup>-</sup> concentration to  $i_{corr}$  was only 2%. This is because the restricted oxygen levels caused a significant slowing of local corrosion. At the same time, temperature also reduces the corrosion acceleration effect of Cl<sup>-</sup> [39]. The contribution of each environmental factor to the elevated i<sub>corr</sub> under fully oxygenated conditions is shown in Figure 14b. At this point, the Cl<sup>-</sup> [25] concentration played a control role and contributed up to 85% of the increase of icorr. This indicates that the acceleration effect brought about by Cl<sup>-</sup> can only occur under conditions of sufficient oxygen. The study in 3.1 found that the corrosion of ductile iron intensified because of the severe localized corrosion caused by the concentration cell effect, and the results of the kinetic law analysis here also confirmed this. The continued dissolution of the anode under conditions of sufficient oxygen causes  $Cl^{-}$  to continue to diffuse into the slit between the graphite and the cast iron, exacerbating the corrosion of the ductile iron. this is why the i<sub>corr</sub> contribution is so high.

Figure 14c shows the contribution of environmental factors to the  $i_{corr}$  of ductile iron after eliminating obvious defects on the surface. It can be deduced that the influence effect of each environmental factor becomes uniform. This means that, under this condition, the effect of the deterioration of the water quality environment on the corrosion acceleration of ductile iron is obviously weakened; moreover, the oxygen concentration is not a highly influential environmental factor, but the contribution rate is still high. This may be the

reason for the weakening of the local corrosion effect. Under fully oxygenated conditions, the contribution of Cl<sup>-</sup> concentration to  $i_{corr}$  suddenly decreases. This indicates that, as the degree of local corrosion decreases, Cl<sup>-</sup> concentration is no longer the most important environmental factor affecting  $i_{corr}$ . However, pH and immersion time contributed to the increase in  $i_{corr}$ , which may be due to the fact, that the originally flat surface of the mechanically treated ductile iron samples gradually exhibited more defects as the corrosion progressed, leading to increased localized corrosion. However, it still corrodes less than ductile iron without any surface treatment. For temperature and water hardness, the  $i_{corr}$  contribution did not change significantly before and after mechanical treatment under fully oxygenated conditions. This indicates that an increase in temperature from 60 °C to 90 °C does not bring about a significant increase in localized corrosion.



**Figure 14.** Analysis of the contribution of environmental factors to i<sub>corr</sub>. (**a**,**c**) show the contribution of non-surface-treated ductile iron in all environments and in fully oxygenated conditions, respectively; (**b**,**d**) show the contribution of the surface-treated ductile iron in all environments and in fully oxygenated conditions, respectively.

### 4. Conclusions

(1) Defects such as pores and shrinkage generated in the process of producing ductile iron easily become a gathering place for aggressive ions, which induce the dissolution of graphite spheres and the matrix interface, and then induce serious local corrosion. After surface mechanical treatment to eliminate holes and shrinkage, SEM observations and CLSM statistics of the pits show that localized corrosion pits on the material surface are significantly suppressed. The average i<sub>corr</sub> in the different solutions is lower and the corrosion kinetic processes are inhibited. All of the results prove that surface treatment techniques can improve the corrosion resistance of ductile iron, and inhibit localized corrosion.

(2) Simulations revealed that the solution around graphite spheres for defects such as pores and shrinkage loosening is highly susceptible to acidification, whereby an acidification autocatalytic cell effect is formed, accelerating the dissolution of the substrate and reducing the corrosion resistance of the material.

(3) Electrochemical test results showed that changes in water quality have a greater impact on the corrosion kinetic process of ductile iron. For unsurfaced ductile iron, the

order of the relative weight of the environmental factors that affect corrosion resistance in all environments is oxygen solubility > temperature > water hardness > immersion time > pH >  $Cl^-$  concentration. Under oxyfuel conditions, the order of the relative weight of the environmental factors that affect corrosion resistance is  $Cl^-$  concentration > water hardness > immersion time > pH > temperature.

(4) For surface-treated ductile iron, with the removal of obvious defects from the ductile iron's surface, oxygen concentration is no longer the main factor in determining the  $i_{corr}$  value. Under oxyfuel conditions, the immersion time becomes the largest factor affecting the  $i_{corr}$  contribution, not Cl<sup>-</sup> or pH. This indicates that uniform corrosion emerges as the dominant type of erosion as immersion time increases.

**Author Contributions:** Methodology, T.L., K.T. and X.Y.; Software, X.Y.; Validation, T.L.; Formal analysis, T.L. and K.T.; Investigation, L.Z.; Resources, C.L.; Data curation, B.W. and C.L.; Writing—original draft, B.W.; Writing—review and editing, C.L. and X.C.; Project administration, L.Z. and X.C. Funding acquisition, C.L. and X.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** The National Natural Science Foundation of China (No. 52104319); the National Science and Technology Resources Investigation Program of China (No. 2019FY101400).

**Data Availability Statement:** The raw/processed data required to reproduce these findings cannot be shared at this time as the data are related to an ongoing study.

Acknowledgments: The authors acknowledge Qinglin Li and Yunyang Wu in University of Science and Technology Beijing for their assistance in the experiment.

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

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