The Initial Corrosion Behavior of 20# Steel under the CO₂/Aqueous Solution Gas–Liquid Two-Phase Bubble Flow Condition

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Abstract: The initial corrosion behavior of 20# steel under the condition of gas–liquid (CO₂/aqueous solution) two-phase bubble flow was studied through weight loss, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. The results showed that the corrosion rate decreased rapidly when the corrosion time was less than 3 h, increased rapidly, even to 19.4% of the initial corrosion rate, when the corrosion time was from 3 h to 5 h, and then decreased slowly to about 63% of the initial corrosion rate after the corrosion time exceeded 5 h under different CO₂ pressure conditions. The corrosion happened first at the defects area with a high activity such as the cross points of scratches, gradually formed corrosion pits, and then extended around until the corrosion products covered the whole pipe wall surface. At the beginning stage of the corrosion process, the corrosion products were composed of acicular corrosion products and a small number of flocculent corrosion products and formed the corrosion product layer with micro-cracks. With the extension of the corrosion time, the spherical corrosion particles started to form on the initial corrosion product layer’s surface and gradually covered the initial corrosion product layer completely. The whole corrosion product layer with dual-structure characteristics formed. The inner corrosion product sub-layer was composed of initial corrosion products with columnar characteristics from the cross-section perspective, and the outer corrosion product sub-layer was composed of spherical corrosion products that were relatively dense. There was no obvious interface between the inner columnar sub-layer and the dense outer sub-layer. As time went on, the corrosion product particles with a broccoli shape characteristic formed on the dual-structure corrosion product layer’s surface and finally formed the outermost layer of the whole corrosion product layer. In the end, the whole corrosion product layer with three sub-layers formed, namely, the columnar bottom sub-layer, the relatively dense middle sub-layer, and the surface dense sub-layer composed of particles with a broccoli shape. The main components of the corrosion products were Fe, C, and O, and the main phases of the corrosion products were Fe₃C, FeCO₃, Fe₂O₃, Fe₃O₄, and FeOOH.

Keywords: CO₂/aqueous solution two-phase bubble flow; morphology characteristic of a corroded surface; evolution of a corrosion product; corrosion process model

1. Introduction

In recent decades, the demand for oil and gas pipelines and connecting pipelines between the processing devices under various working conditions increased with the rapid increase in the consumption of petrochemical products, especially the rapid development of oil and gas recovery and processing technology [1–3]. Higher requirements have been put forward for the performance of the transmitting pipeline and connecting
pipeline. CO₂ itself is an associated product of oil and gas or an indispensable by-product in the treating process. Therefore, crude oil and gas from an oil reservoir/gas well usually contain a certain amount of CO₂. The CO₂ corrosion problem is very severe for the pipeline. Research reports have shown that the CO₂ corrosion is even more severe than that of strong acids such as H₂SO₄ or HCl under the same pH value conditions [4,5]. CO₂ corrosion can cause thinning, perforating, and cracking of the pipeline or treatment device, which usually leads to the failure of parts and components. The failure of components often results in the shutdown of the entire production line or even the burst of the device or pipeline. Therefore, CO₂ corrosion is a prominent and severe problem in transmitting pipelines and petrochemical treating devices [5–7]. At present, researchers at home and abroad have conducted more studies on CO₂ corrosion, including static corrosion in a CO₂ saturated solution at a normal pressure, corrosion at different temperatures, CO₂ corrosion under different pressure conditions in a high-pressure reactor, and CO₂ corrosion under dynamic conditions formed through the installation of a stirring device in the reactor. However, there are many influencing factors for the actual corrosion of petrochemical plants and pipelines, such as the pressure, the temperature, the flow rate of the medium in the device or pipelines, the composition and wettability of the medium, the surface state conditions, etc. The interaction of these factors is very complex. Relevant scholars believed that the CO₂ corrosion was fundamentally related to the interaction between anode reaction and cathode reaction in the corrosion process [8–10]. Nesci [11] studied the electrochemical and chemical reaction mechanisms of CO₂ corrosion on metals. According to the experimental results, the molecular CO₂ was directly adsorbed on the metal surface during the corrosion process, forming a chemical ligand to replace the iron hydroxide intermediate and then actively participating in the electrochemical process of iron dissolution. Other studies showed that the cathodic reaction below 90 °C was considered to be the reduction of H⁺, HCO⁻, HCO₃⁻, and H₂O, where H₂CO₃ and HCO₃⁻ promoted the cathodic reaction through the buffer effect. They decomposed on the steel surface to produce H⁺ and then participated in the reaction process to precipitate hydrogen. The actual petrochemical devices and pipelines would be running under a certain pressure, flow rate, temperature, and other technical conditions because of the transmitting requirements and treating process requirements. These actual technical parameters would cause two-phase or multi-phase coexistence in petrochemical devices or pipelines. Under different pressures and flow velocity conditions, the flowing medium in the device and pipeline would present a variety of different flow states, i.e., the flow pattern. For the gas–liquid two-phase medium, bubble flow, slug flow, wavy flow, annular flow, and stratified flow were usually formed. The actual service conditions of pipelines or devices were relatively more complex. In order to maximize the consistency between the experimental conditions and the actual service conditions, researchers mostly used self-designed equipment to simulate the actual service conditions and study their corrosion behavior. Some scholars [12] reported that the gas in gas–liquid two-phase slug flow was entrapped in the form of scattered bubbles. The dispersed bubbles pushed to the bottom of the pipeline burst and caused an effect of similar cavitation, which could damage or even remove the protective layer or corrosion product layer. The corrosion would be intensified under the bubble cavitation and fluid shear stress conditions. Li et al. [13] studied the relationship between the bubble cavitation model and multiphase slug flow. It was found that the dispersed bubbles in multiphase flow acted on the pipe wall surface to promote or aggravate the damage of the surface layer, and the damage intensity was related to the density of bubbles. The shear stress on the pipe wall surface was also measured in this study, which indicated that these stresses were not only surface stresses caused by liquid flow but were directly related to the additional shear stresses cause by slug flow. Liu et al. [14] numerically simulated the gas–liquid two-phase bubbly flow in a straight pipe. Four kinds of forces between the continuous liquid phase and bubble were considered in the model: the resistance force, lift force, turbulent dispersion force, and wall force. The study results showed that the resistance force would make the bubble move along the mainstream
direction, the lift force would make the bubble move towards the wall, and the wall force would make the bubble move far away from the wall. The combined effect of the lift force and wall force would make the volume fraction of the gas phase reach the peak near the wall. Other researchers [15,16] have studied the complex bubble deformation and break-up dynamics using the interface capturing approach, the efficient simulation of bubble dispersion, and the resulting interaction. In these studies, only gas–liquid two-phase separation, bubble deformation and dispersion, and its break-up dynamics or interaction were involved, but their effect on corrosion behavior was not involved. Zhang et al. [17] found that the alternating load generated during the slug flow fluctuation process could make the corrosion product layer fail and aggravate the local corrosion. Song et al. [18] studied the corrosion behavior of 20# steel in CO$_2$/aqueous gas–liquid two-phase plug flow, and the results showed that the corrosion product characteristics of the upper and bottom wall of the pipe were different. Villar Real [19] found that the larger shear stress on the pipe wall would destroy the corrosion product film in the plug flow with a high turbulence intensity. So far, the corrosion models in the flowing medium related to the flow effect could be divided into four types: mass transfer, phase transfer, erosion wear, and cavitation corrosion. However, these models are based on a certain factor during the corrosion process, and these models still could not provide reliable help for the corrosion behavior evaluation or corrosion prediction of devices or pipelines in actual service.

It can be seen from the above discussion that there are not systematic reports on the corrosion behavior of gas–phase two-phase bubbly flow, but the bubbly flow is inevitable in petrochemical plants and pipelines. The corrosion behavior and mechanism of the plant or pipeline under the bubbly flow state are very important for the safe operation of the whole plant or pipeline. The corrosion behavior and mechanism of a 20# seamless steel pipe under bubbly flow conditions are still unclear. Therefore, the corrosion behavior of the 20# seamless steel pipe in CO$_2$/aqueous solution gas–liquid two-phase bubbly flow was systematically studied through the self-designed pipeline platform simulating the actual bubbly flow in the pipeline. The changes in the corrosion rate, the corrosion morphology and the microstructure of the corrosion product layer, as well as the corrosion product composition, were mainly analyzed. The corrosion process model was put forward under the above study results and analysis. Although this corrosion process model was put forward based on the gas–liquid two-phase bubbly flow state, it is meaningful for dynamic corrosion research. This would provide a theoretical basis for corrosion evaluation and corrosion prediction under the actual service conditions.

2. Experimental

The experimental material, the sample size, and its treating process are same as those in references [20] and [21]. The corrosive medium is the same as that in references [20] and [21]. The experimental condition was a gas–liquid two-phase (CO$_2$/aqueous solution) bubbly flow at room temperature. According to the Mandhane flow type figure, the liquid velocity and gas velocity were set as 0.72 m s$^{-1}$ and 0.36 m s$^{-1}$, respectively. Figure 1 is the sketch of the self-designed corrosion experimental platform simulating gas–liquid two-phase flow in the pipeline. The CO$_2$ pressure was set at 0.04 MPa, 0.10 MPa, and 0.15 MPa by adjusting the valve, respectively. The samples in this study were divided into ten groups; the corresponding test time of each group was 10 min, 20 min, 40 min, 2 h, 3 h, 4 h, 5 h, 7 h, and 9 h, respectively. The treatment and analysis of the samples after the corrosion are the same as those in references [20] and [21]. The method for the observation of the surface morphology and composition analysis of the corrosion products is the same as that in references [20] and [21].
3. Results and Discussion

3.1. Corrosion Rate

Figure 2 shows the corrosion rate curve of 20# steel under certain velocities of liquid and gas ($V_L = 0.72 \text{ m/s}$, $V_g = 0.36 \text{ m/s}$) and different CO$_2$ pressure conditions with time at room temperature. As can be seen in Figure 2, the corrosion rate under different CO$_2$ pressure conditions decreased rapidly with time at the beginning stage of corrosion, reached the minimum value at 3 h, and then gradually increased with time to reach the peak value of experimental conditions at 5 h. After 5 h, the corrosion rate decreased gradually and then tended to be nearly unchanged. Figure 2 shows that the deviation of the corrosion rate decreased gradually with the corrosion time under different CO$_2$ pressure conditions. When the CO$_2$ pressure was 0.1 MPa, the corrosion rate reduced to 0.55 mm/a at 3 h and increased to 2.68 mm/a at 5 h from the changing curve of the corrosion rate, as seen in Figure 2. The peak value at 5 h was still lower than that at 10 min. However, the minimum corrosion rate was about twice that of 0.254 mm/a according to the NACE RP-0775-91 standard, which is basically a serious corrosion [22]. This criterion for corrosion determination is obtained under static corrosion conditions. Therefore, the corrosion of vessels, pipelines, or equipment in the flow medium is far more serious than that in the static state, that is, the corrosion data or analysis results under the static state condition could not be directly applied to the corrosion evaluation, the corrosion prediction, and the risk assessment of equipment in service under actual dynamic conditions.
3.2. Morphology of the Corroded Surface

The changing trends of the corrosion rate under different CO₂ pressure conditions are similar, as seen in Figure 2. In order to further analyze the corroding process and forming mechanism of corrosion products, the micro-structure and composition of corrosion products with time under a 0.1 MPa CO₂ pressure condition were systematically analyzed. Figure 3 shows the evolution process of the corroded microstructure of 20# steel with time at room temperature when the liquid velocity and gas velocity are 0.72 m/s and 0.36 m/s, respectively. As can be seen in Figure 3, the black-gray area (as shown in the circle area in Figure 3a–g and the light-gray area (as shown in the rectangular area in Figure 3a–g could be observed in the microscopic morphology of the corroded pipe wall surface. However, the size of the black-gray area and the light-gray area varied with time. Only a small amount of black-gray corrosion products formed on the pipe wall surface when the corrosion time was 10 min. The black-gray corrosion product was discontinuous, as shown in Figure 3a. A corrosion pit appeared in the center of every black-gray area. The clear scratches could be seen in the light-gray area far away from the black-gray area, as shown in the rectangular area of Figure 3a. When the corrosion time was 20 min, the number of corrosion products increased significantly in the black-gray area, and the scratches had become less noticeable in the light-gray area, as shown in Figure 3b. This indicated that there were corrosion products also covered in the light-gray area. At this moment, the corresponding corrosion rate decreased, as shown in Figure 2. The black-gray area gradually expanded with corrosion time. The number of corrosion pits in the black-gray area increased obviously, and the corrosion pit appeared gradually in the light-gray area, as shown in Figure 3c,d. Meanwhile, the corrosion pits appeared in a connecting and expanding trend. The residual scratches of the surface pretreatment in the light-gray area gradually disappeared with corrosion time. When the corrosion time was 2 h, the density of corrosion pits in the light-gray area reached the maximum, as shown in Figure 3e. The corrosion products centered on pits extended further and gradually connected with the surrounding corrosion products with corrosion time. When the corrosion time was 3 h, except for a small number of concentrated black-gray aggregated corrosion products, most of the pipe wall surface presented the gray spot characteristics, the pipe wall surface was relatively smooth, and the corrosion pits gradually decreased from the corroded surface, which indicated that the pipe wall has been completely covered by corrosion products, as shown in Figure 3f. The corrosion rate reached the minimum at 3 h, as shown in Figure 2. The whole pipe wall surface presented a deep gray color, and there were black-gray corrosion products at the local area when the corrosion time was further prolonged. When the corrosion time was 4 h, the corrosion pits connected or their diameter increased, as shown in Figure 3g, which resulted in an increasing corrosion rate, as shown in Figure 2. As the corrosion was going on, the corrosion product layer on the pipe wall surface was becoming thicker and denser, and serious micro-cracks appeared in the corrosion product layer at 5 h. At this moment, the “mushroom-like” convex cells appeared on the corrosion products film surface, as shown in Figure 3h. The thickness and density of the corrosion product layer increased significantly, which could be confirmed from the area where the crack of the corrosion product layer turned up, and part of the corrosion layer peeled off. The area where cracks and spalling occurred was the black-gray area at the beginning stage. However, the cracking and peeling made the corrosive solution fully contact with the fresh pipe wall, which led to a further increase in the corrosion rate. For the light-gray area at the beginning stage, there was a smooth and relatively dense corrosion product layer formed at 5 h, as well corrosion pits with a larger diameter and little spalling or micro-cracks around the corrosion pits, as shown in Figure 3i. When the corrosion time was 7 h, the density of the corrosion products layer in the black-gray area further increased, and there were still micro-cracks existing in the corrosion layer. However, the micro-cracks at 7 h were sparse, and the surface corrosion product layer was smoother than that at 5 h, as shown in Figure 3j. For the light-gray area at the beginning stage, the “mushroom like” corrosion product cells also appeared at 7 h, as shown in Figure 3k, and
its diameter was relatively smaller. The corroded morphology characteristic in Figure 3k was similar to that in Figure 3h, which indicated that the corrosion process in the light-gray area was later than that in the black-gray area. The corrosion rate decreased owing to the increasing density of the corrosion products layer and the fewer micro-cracks, that is, the corrosion process was slowed.

Figure 3. The micro morphology of the pipe wall surface after different corrosion times: (a) 10 min, (b) 20 min, (c) 40 min, (d) 80 min, (e) 2 h, (f) 3 h, (g) 4 h, (h) and (i) 5 h, (j) and (k) 7 h.

Figure 4 shows the magnified morphology of the black-gray area in the circle area of Figure 3. Figure 4a,c,e,g,i,k,m,o,q show the low-magnified morphology of the corrosion products, and Figure 4b,d,f,h,j,l,n,p,r show the corresponding further magnified
morphology. When the corrosion time was 10 min, the remaining scratches in the pre-treatment process were seen clearly, as shown in Figure 4a, although there were white particles scattered on the corroded surface. After further magnifying the local area, as shown in Figure 4b, the fine needle-like corrosion products were uniformly distributed on the corroded surface, and its length was less than 0.5μm. When the corrosion time was 20 min, there was an obvious corrosion layer formed, gray-white flocculent products formed on the corrosion products surface, and a very thin layer of approximate transparent corrosion product covered away from the needle-like corrosion products area, as shown in Figure 4c. The local area was further magnified, as shown in Figure 4d; it showed that the gray-white flocculent products were composed of even finer needle-like corrosion products, and the flocculent products made the transparent layer crack. More scattered gray-white flocculent products formed on the surface of the needle-like corrosion products layer, as shown in Figure 4e, with time. The gray-white flocculent products were composed of much finer needle-like corrosion products, as shown in Figure 4f. With the further extension of corrosion time, the corrosion product layer was further densified, and the gray-like flocculent product increased, as shown in Figure 4g,i. The reticular micro-cracks appeared in the corrosion product layer, as shown in Figure 4h,j. When the corrosion time reached 3 h, the pipe wall was entirely covered by corrosion products, and the flocculent products gradually became a flower bud shape that seemed to open at the cracks area and densify gradually. After that, the corrosion products with a flower bud shape continued to form on the corrosion products surface, as shown in Figure 4k. There were a small number of micro-cracks in the local area of the corrosion product layer, and some of them were filled with the subsequent corrosion products, as shown in Figure 4l. At this moment, the corrosion product layer with a dual-structure characteristic had been forming, and the corrosion product layer was composed of an intensive deposition acicular sub-layer and a flocculent product sub-layer. The corrosion rate reached the minimum value of the experimental condition at this moment because the coverage rate and density of corrosion products increased obviously. Figure 4m shows the microstructure of the corroded surface at 4 h, which indicated that there were many white spherical particles covered on the corrosion product surface. The white flocculent corrosion products aggregated to form these white spherical particles. Its local further magnified morphology is shown in Figure 4n. Compared with Figure 4l, the whole corrosion product layer in Figure 4n had deeper and wider penetrating micro-cracks, and the micro-cracks became less numerous, which still provided a free channel for the diffusion of corrosive ions. It could be seen that the corrosion rate increased slightly at this time, as shown in Figure 2. When the corrosion time was extended to 5 h, the shape of the fine spherical corrosion particles on the corrosion products surface transformed into a “broccoli” shape with a diameter of about 10 μm, as shown in Figure 4o. Its further magnified morphology showed that the broccoli shape corrosion products were composed of gathered tiny white spherical particles, as shown in Figure 4p, and it was confirmed by the scattered white spherical particles near the broccoli corrosion products as the arrows. There were penetrated net-like micro-cracks in the corrosion product layer, which provided a more unobstructed diffusing channel for corrosive ions. This made the corrosion rate increase significantly, as shown in Figure 2. As the corrosion time continued to extend, the micro-cracks became the priority area for corrosion products deposition. Therefore, the broccoli corrosion products became much denser, as shown in Figure 4q. Its further magnified morphology is shown in Figure 4r, which showed that the micro-cracks became less numerous and the width of the micro-cracks became hard to see compared with that in Figure 4p. Until this moment, a composite corrosion product layer consisting of a dense outer layer composed of broccoli-shaped corrosion products and an inner layer with a dual structure characteristic had been formed. This characteristic of the corrosion product layer played a strong role in inhibiting the corrosion dynamics process, namely, the corrosion rate decreased significantly, as shown in Figure 2.
Figure 5 shows the magnified morphology of the light-gray area in the rectangle of Figure 3. A small number of loose flocculent and acicular corrosion products formed on the pipe wall surface in a short time, as shown in Figure 5a. The residual scratches of the surface pretreatment were clearly visible, as shown in the upper-right corner figure of Figure 5a, and the flocculent and acicular corrosion products deposited preferentially at the scratches area, especially at the deep scratch or their crossing area. As time was going on, the number of loose flocculent and acicular corrosion products increased, as shown in the upper right corner figures of Figure 5b,c. It can be seen from Figure 5b,c that the flocculent corrosion products aggregated by tiny needle-like products. The initial needle-like corrosion products were easy to float in the gas-liquid two-phase bubble flow and then adsorbed each other to form the cluster in the floating process. However, the smaller flocculent corrosion products cluster was also easy to be washed, as shown in the upper-right corner figure of Figure 5d. The flocculent corrosion products floating were also easy to absorb near the corrosion pits and were retained locally, as shown in Figure 5d. When the corrosion time was further prolonged, the flocculent and acicular corrosion products continued to increase and aggregate. The corrosion product cluster would be stably retained and grew when the corrosion products aggregation reached a certain size, as shown in the upper-right corner figures of Figure 5e,f. The corresponding further magnified morphology is shown in Figure 5e,f. It can be seen that the light-gray area had been completely covered by corrosion products when the corrosion time reached 3 h. However, the corrosion product layer at the light-gray area was much thinner than that at the black-gray area. A small number of flocculent corrosion products continued to deposit on the surface of the acicular corrosion product layer. By comparison, it was found that the morphology characteristic of the light-gray area in Figure 5f was similar to that of the black-gray area in Figure 4f, which indicated that the corrosion process in the light-gray area lagged behind that of the black-gray area. The upper-right corner figure of Figure 5g shows that the corrosion products composed of loose honeycomb particles formed in the light-gray area when the corrosion time was 4 h. Its further magnified morphology is shown in Figure 5g, which showed that the loose honeycomb particles were composed of flocculent particles that were aggregated by acicular corrosion products. The surface of the loose honeycomb particle was rough and uneven, accompanied by local corrosion products peeled off. The porosity of the corrosion product was larger, as shown in Figure 5g, which resulted in the increase in the corrosion rate at 4 h in Figure 2. When the corrosion time was 5 h, the surface of the corrosion product in the light-gray area was relatively smooth and clean, and the corrosion product layer was relatively dense. However, there were network-connected micro-cracks in the corrosion product layer, as shown in the upper-right corner figure of Figure 5h under low magnified conditions. Its further magnified morphology is shown in Figure 5h, which indicated that its morphology characteristic was similar to that
of the black-gray area after 80 min of corrosion, as shown in Figure 4h. Although the corrosion product layer was relatively dense, the network micro-cracks made the corrosive ions easily reach the pipe wall fresh surface through the micro-cracks, which led to the increase in the corrosion rate. When the corrosion time was 7 h, the corrosion product layer was becoming relatively dense, and there were some local micro-cracks in it. At this moment, there were also flocculent corrosion products distributing discretely on the surface of a relatively dense corrosion product layer, as shown in the upper-right corner figure of Figure 5i. It can be clearly seen from its local magnified morphology that the white loose flocculent corrosion products covered on the surface of a relatively dense corrosion product layer, as shown in Figure 5i. This morphology characteristic was similar to that of the black-gray area when the corrosion time was 2 h, as shown in Figure 4k. It was found that the evolution of corrosion products at the light-gray area lagged behind that at the black-gray area, which further confirmed the formation process of the corrosion product layer with dual micro-structure characteristics at the black-gray area. That is, the needle-like flocculent corrosion products deposited preferentially at the scratch area, especially at the cross of scratches or the cross of scratch and impurity. With the extension of the corrosion time, the corrosion products at the initially corroded surface could continuously grow and become the stable nucleation area for the continuous deposition and growth of corrosion products. The corrosion product layer was becoming thicker and denser during the process of the corrosion product layer spreading around. The micro-cracks would appear when the relatively dense corrosion product layer grew to a certain extent; at the same time, the spherical flocculent corrosion products formed on its surface. The inner corrosion product layer with a dual-microstructure characteristic was forming when the spherical flocculent corrosion products accumulated to a certain extent. Afterwards, the dispersed corrosion products with a broccoli shape began to form on the corrosion product layer surface with a dual-microstructure characteristic. The corrosion products with a broccoli shape continued to grow until forming the new dense outer layer with time. In this way, the whole corrosion product layer composed of an inner layer with a dual-structure characteristic and a relatively dense outer layer was forming.
Figure 5. The morphology of corrosion products at the light-gray area under different corrosion time conditions: (a) 10 min, (b) 20 min, (c) 40 min, (d) 80 min, (e) 2 h, (f) 3 h, (g) 4 h, (h) 5 h, (i) 7 h. (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 are the EDS scanning points.)

Figure 6 shows the local appearance of corrosion products at the black-gray area under different corrosion time conditions. The local morphology was the in situ cross-section morphology of the corrosion products with a certain angle due to the cracking or warping of the corrosion product layer during the formation process. Figure 6a shows the local morphology after 5 h of corrosion, which showed that the corrosion products layer presented a dual-microstructure characteristic. The inner layer looked relatively dense, as shown in the area between the red dotted lines. The outer layer was composed of spherical flocculent corrosion products, shown as the white arrow, and the outer layer had not completely covered at this time. The exposed fresh pipe wall could be observed at the peeling or stripping area, which resulted in the significant increase in the corrosion rate. The inner layer in the area between the red dotted lines was further magnified, as shown in Figure 6b. It could be seen that the inner layer presented a dual-structure characteristic. It was composed of a columnar sub-layer and a relatively dense sub-layer. The columnar sub-layer was perpendicular to the pipe wall, and the dense sub-layer composed of needle-like corrosion products was laid on the columnar sub-layer surface. When the corrosion time was 7 h, the dual-structure characteristic of the inner layer was more obvious, as shown in Figure 6c. The thickness and density of the inner layer increased, and the coverage rate of the outer layer also increased accordingly. The spherical flocculent corrosion products gradually took on a broccoli shape, and its density increased. At this moment, the peeling off or micro-cracks of the corrosion product layer decreased compared with that at 5 h, and the corrosion rate decreased. The fracture local morphology of the corrosion product layer owing to the warping was further magnified, as shown in Figure 6d. The inner sub-layer of the columnar corrosion products and the relatively dense outer sub-layer tiled on it could be clearly seen, and there was no obvious interface between the two sub-layers. Figure 6e shows the crack local morphology of the corrosion product layer when the corrosion time was 9 h. The interface between the two sub-layers became obvious at this time. The delamination phenomenon occurred for the inner layer with a dual-structure characteristic, as shown by the white arrow in the figure. There were penetrated cracks in the inner sub-layer adjacent to the pipe wall, while the network micro-cracks appeared in the outer sub-layer, and the network micro-cracks did not penetrate to the pipe wall surface, as shown in Figure 6f. The particle size of the broccoli corrosion products increased greatly and gradually became the relatively dense outer layer on the surface of the dual-structure inner layer. At the same time, the inner layer with a dual-structure characteristic differentiated into a columnar inner sub-layer and a dense needle-like middle sub-layer. So far, the whole corrosion product layer evolved into a composite layer composed of a columnar inner sub-layer, a dense needle-like middle sub-layer, and a relatively dense broccoli outer sub-layer. Combined with Figure 2, it could be seen that the corrosion rate further decreased because the thickness and density of the corrosion product layer with three sub-layer structure characteristics increased compared with that at 7
h. The thickness of the three sub-layers from the pipe wall surface to the surface of the whole corrosion product surface was about 2 μm, 1 μm, and 0.5 μm, respectively.

Figure 6. The local morphology of corrosion products at the black-gray area under different corrosion times: (a) and (b) 5 h, (c) and (d) 7 h, (e) and (f) 9 h.
3.3. The Composition Analysis of Corrosion Products

3.3.1. EDS Analysis

As shown in Figure 3, the corroded surface at different times presented two kinds of morphology characteristics: the black-gray area centered at corrosion pits and the light-gray area far away from corrosion pits. It can be seen in Figure 4 and Figure 5 that the deposition rate of the corrosion products at the black-gray area was greater than that at the light-gray area. The composition and content of the corrosion products at the black-gray area in Figure 4 with time is shown in Table 1, when the corrosion time was within 2 h. The odd points, such as 1, 3, 5, 7, and 9, represented the corrosion products at a relatively uniform area. The even points, such as 2, 4, 6, 8, and 10, represented the flocculent corrosion products at the protuberance area. Table 2 shows the analysis results of the composition and content of corrosion products with different morphology characteristics at the black-gray area with time when the corrosion time was more than 3 h. Similarly, the points A, C, E, and G represented the corrosion products at a relatively uniform area, while the points B, D, F, and H represented the flocculent corrosion products at the protuberance area. With the extension of corrosion time, the Fe content of the corrosion products at different morphology characteristic areas presented a gradually decreasing trend, while the total content of C and O gradually increased. The evolution of the morphology characteristic of corrosion products with time showed that the density of the corrosion product layer gradually increased with the corrosion time. Table 3 shows the EDS analysis (Japan JEOL LTD.) results of corrosion products with different morphology characteristics with time at the light-gray area in Figure 5. The classification and meaning of all points were same as those in Table 1. The content change trends for Fe, C, and O in corrosion products with different morphology characteristics with time were the same as those in the corresponding characteristic corrosion products at the black-gray area. The Fe content of uniform corrosion products at the light-gray area was higher than that at the black-gray area under the same corrosion time condition. The Fe content in the inner corrosion product sub-layer was higher than that in the outer corrosion product sub-layer. The change trend of the total content of C and O was the opposite to that of Fe. The composition and content of corrosion products at the light-gray area after 7 h of corrosion were basically same as those at the black-gray area after 2 h of corrosion. It was confirmed again that the corrosion process at the light-gray area lagged behind that at the black-gray area from the perspective of the composition and content of the corrosion products.

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<th>7 H</th>
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Table 1. The main elements and content in corrosion products at the black-gray area under different corrosion times within 2 h (wt.%).

Table 2. The main elements and content in corrosion products at the black-gray area under different corrosion times beyond 3 h (wt.%).
Table 3. The main elements and content in corrosion products at the light-gray area after different corrosion times (wt.%).

<table>
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3.3.2. XRD Analysis

Figure 7 shows the XRD diffraction (JEOL LTD, Tokyo, Japan) pattern of corrosion products under different corrosion time conditions when the CO$_2$ pressure was 0.1 MPa, which showed that the main phases of corrosion products were Fe, Fe$_3$C, FeCO$_3$, FeOOH, FeO$_2$, and FeOOH. This result was also consistent with the EDS results. The microstructure of the 20# steel used in the experiment is ferrite and pearlite, and α-Fe and Fe$_3$C are the main phases. The main components of the corrosion products are iron oxides and carbonates. The cementite Fe$_3$C did not participate in the chemical reaction during the corrosion process, and it might be retained in situ or flow into the liquid with the Fe dissolution. The retained Fe$_3$C might become the substrate or skeleton for the deposition of corrosion products. FeOOH is hydroxyl iron (goethite), which easily formed the porous structure during deposition. Therefore, it could be inferred that the needle floccule formed on the corroded surface might contain hydroxyl ferric oxide. The existence of FeO$_2$ and FeOOH in corrosion products indicated that the oxidation was accompanied in the corrosion process. With the extension of corrosion time, the diffraction peak of Fe decreased gradually. The thickness and density of the corrosion product layer gradually increased with time, which resulted in the gradual weakening of the diffraction information of Fe.

![XRD pattern](image)

Figure 7. The XRD pattern of the corrosion products at 0.1 MPa CO$_2$ pressure under different corrosion time conditions.

3.3.3. XPS Analysis

Figure 8 shows the XPS (JEOL LTD, Tokyo, Japan) spectrum of corrosion products under different corrosion time conditions in gas–liquid two-phase bubble flow. Figure 8a,c,e,g showed the binding energy of corrosion products at 2 h. Figure 8b,d,f,h showed the binding energy of corrosion products at 7 h. Figure 8a was the full binding energy spectrum at 2 h, and the peaks of core potentials of C1s, O1s, and Fe2p in the corrosion products could be detected. The binding energy of C1s was 284.8 eV, as the calibration value. The charge shift was corrected by the adsorption peak of C1s, and the Gauss Lorentz curve was used to fit the peak. There were three energy spectrum peaks at BE =
284.49 eV, BE = 285.15 eV, and BE = 288.45 eV for C1s, as shown in Figure 8c, which corresponded to FeC and FeCO3, respectively. There were three energy spectrum peaks at BE = 529.84 eV, BE = 530.81 eV, and BE = 531.88 eV for O1s, as shown in Figure 8e, which corresponded to FeO3, FeOOH, and OH, respectively. There were two energy spectrum peaks at BE = 711.09 eV and BE = 713.77 eV for Fe2p3 and one energy spectrum peak at BE = 724.74 eV, as shown in Figure 8g, which corresponded to FeO4, FeOOH, and FeO3. The results of the XPS analysis showed that the corrosion product layer of 20# steel in gas–liquid two-phase bubble flow was composed of FeC, FeCO3, FeO3, FeO4, and FeOOH with the corrosion time. It was found that the diffraction peaks of Fe became weaker, the diffraction peaks of C and O became stronger, and the peak values were roughly not changed in the fine spectrum of each element. The contents for every kind of corrosion product were changed with time. The relative content of FeCO3 and FeOOH increased with time, as confirmed by Figure 8c,d and Figure 8e,f.
4. Analysis and Discussion

In this research, the corrosion behavior of 20# steel in CO$_2$/aqueous solution gas–liquid two-phase bubble flow was studied by using a self-designed dynamic corrosion platform. The corrosion rate of 20# steel in the CO$_2$ aqueous solution depended on the flow characteristic of the gas–liquid two-phase flow and electrochemical corrosion process. The sketch model of the corrosion process was established based on the changing trend of the corrosion rate, the corrosion morphology characteristic, the elements, and the composition analysis results of the corrosion products, as shown in Figure 9. The higher initial corrosion rate was due to the rapid formation of corrosion products on the whole pipe wall when the corrosive medium contacted with the fresh pipe wall surface. The corrosion first started from the high active area, such as crystal defects, point impurities, cross points of scratches, and so on, which could be confirmed through Figures 4a and 5a. The corrosion products at the initial stage were acicular flocculent, as shown in Figure 9a. The acicular flocculent corrosion products on the pipe wall surface were easy to drift owing to the shear stress of flowing liquid. The acicular flocculent corrosion products could adsorb each other and accumulate during the drift process, and they would be adsorbed and deposited near the corrosion pits when they gathered to a certain extent. The corrosion products spread rapidly around the corrosion pits and gradually thickened. The relatively dense corrosion product layer formed at the initial active area of the pipe wall when the corrosion time was further extended. Meanwhile, the smooth area with a sparse defect density and relatively low reactivity formed a few corrosion products, and this area was the light-gray area that was mentioned before. The corrosion process at the light-gray area lagged behind that of the black-gray area. The corrosion rate decreased with the increasing covering rate of the corrosion product layer and its thickness. The electrode potential of Fe:C is much higher than that of ferrite in 20# steel, which is beneficial to the formation of the galvanic cell between Fe:C and ferrite. The formed galvanic cell, in turn, aggravated the corrosion dissolution of ferrite. The ferrite and cementite in the pearlite are layered and interlaced, which further aggravated the corrosion and dissolution process of Fe [23,24]. The dissolution of ferrite made the Fe:C partially expose and then become the core of deposition for corrosion products or the framework of the corrosion product layer. The dissolution of ferrite might also cause the adjacent Fe:C to loosen and mix into the flowing liquid, which resulted in the formation of corrosion pits. The corrosion pits also became the deposition core of corrosion products, and the corrosion around the corrosion pits would be further aggravated. Therefore, the corrosion product layer formed at these areas with priority. The local turbulence would form when the liquid flowed through the pits,
steps, or bulge area. The local turbulence, in turn, promoted the local corrosion [25–29]. In addition, the area covered by corrosion products and the smooth area with an initial low activity also constituted the cathode and anode of the primary cell, which accelerated the corrosion process of the initial low active area. At the same time, the covering rate of the corrosion products layer was obviously improved, as shown in Figures 4(k) and 5(f). The pipe wall surface was nearly completely covered by the corrosion products, and the corrosion rate reached the minimum value of this experimental condition, as shown in Figure 2. During the corrosion process, the needle-like corrosion products deposited initially on the pipe wall surface, and then the flocculent corrosion products deposited and accumulated on the surface of the needle-like corrosion products. Therefore, the corrosion product inner layer with a dual-structure characteristic formed, as shown in Figure 9b. The density of the corrosion product layer increased with time. The crystal structure of the corrosion products was different from that of 20# steel, which resulted in the formation of internal stress on the interface and among the corrosion product layer. Therefore, the network micro-cracks among the corrosion product layer appeared to relieve internal stress. There was dissolved oxygen in the CO2 aqueous solution, and the electrode potential of oxygen is much higher than that of hydrogen. Therefore, oxygen consumption corrosion was more likely to occur than hydrogen evolution. The oxygen vacancies would gather at the interface between the metal and corrosion product layer when the concentration of oxygen vacancies increased on the surface of the corrosion product layer, and these vacancies entered the metal phase more slowly than they passed through the corrosion product layer. The accumulation of oxygen vacancies could also lead to internal stress, which further led to the rupture and formation of micro-cracks in the corrosion product layer [30]. Some studies have also shown that the low fracture toughness of the corrosion product layer might be the cause of the crack in dynamic corrosion conditions [31]. The corrosion pits would increase with time, as confirmed by the microstructure evolution shown in Figure 3. The corrosion products would precipitate on and around the pits with the corrosion process going on, and the pits would be enlarged, as shown as in Figure 3i. Therefore, the under-deposit corrosion happened, which also resulted in internal stress. At this time, it can be seen in Figure 4o that there were many network micro-cracks and warping in the inner layer, which greatly reduced the ions exchange resistance. Therefore, the corrosive medium could easily contact with fresh metal rapidly, and the corrosion rate increased obviously. The outermost corrosion product layer formed on the surface of the inner layer with dual-structure characteristics owing to the ion fast transfer exchange. The outermost layer was composed of gathered spherical flocculent corrosion products. There were even and large interspaces between the spherical particles composed of flocculent corrosion products, as shown in Figure 9c. The spherical particles of corrosion products agglomerated into a broccoli shape when the time further extended to 5 h. The inner layer with a dual-structure characteristic was composed of a columnar sub-layer growing perpendicular to the pipe wall surface and the thin-dense sub-layer shown in Figure 6a,b. Figure 9d–f show the sketch map of the whole corrosion products layer. The outermost corrosion product particles with a broccoli shape increased and formed a thicker and uniformly distributed corrosion products layer when the corrosion time extended to 7 h. Meanwhile, the corrosion deposition happened in the micro cracks according to the principle of proximity in the transmission process for the corrosive ions and Fe2+, which resulted in the filling of micro-cracks and the increasing density of the corrosion product layer. At this time, the thickness and density of the inner corrosion products layer further increased, as shown in Figure 6c,d, and the sketch map is shown in Figure 9e. The surface of the corrosion product layer presented a compact spherical particles morphology without any cracks, which effectively hindered the exchange of active ions, as shown in Figure 4q. The kinetics process of the corrosion reaction was strongly inhibited, and the corrosion rate decreased significantly. The thickness and density of the outermost corrosion layer composed of spherical particle corrosion products further increased when the corrosion time was 9 h. The inner layer with a dual-structure characteristic became much denser,
and the dual-structure interface became obvious among the inner layer, as shown in Figures 6e, f and 9f. The corrosion rate further decreased, as shown in Figure 2. The corrosion product layer evolved from the inner layer with a dual-structure characteristic and the outermost layer composed of spherical particles into the whole corrosion product layer with three sub-layers when the corrosion time was from 3 h to 9 h. The three sub-layers were a relatively dense columnar inner sub-layer, a dense middle sub-layer, and an outermost sub-layer composed of spherical particles. The area with a relatively smooth morphology and activity corroded lightly and covered with fewer corrosion products as the beginning corrosion. This area was the light-gray area mentioned before. The loose needle-like corrosion products formed at the beginning of the corrosion process, and the pipe wall surface was not completely covered by the corrosion products. When the corrosion time exceeded 3 h, the corrosion product layer had completely covered the pipe wall surface and gradually densified. Their morphology characteristic was similar to that of the black-gray area at 40 min of corrosion. When the corrosion time exceeded 7 h, a layer of white flocculent corrosion products composed of fine needle-like products formed on the surface of the initially formed product layer. The inner layer was relatively dense, and the outer layer was loose; there was no obvious interface between the inner layer and the outer layer. This was the inner layer with a dual-structure characteristic that was mentioned before. Its morphology characteristic was consistent with that of the black-gray area at 2 h of corrosion. The corrosion process at the light-gray area further confirmed the formation process of the inner layer with a dual-structure characteristic in the black-gray area.

![Schematic diagram of the formation process model of the corrosion products layer](image)

**Figure 9.** Schematic diagram of the formation process model of the corrosion products layer: (a) the loose needle and flocculent corrosion products, (b) the needle and flocculent corrosion products gradually densified, (c) the inner layer with dual-structure characteristics and the outer layer composed of spherical particles, (d) the outer layer with a broccoli shape formed, (e) the inner, middle, and outer three sub-layers were gradually densified, (f) the three-layer-structure characteristic corrosion products layer.

5. Conclusions

1. With the extension of the corrosion time, the corrosion rate of 20# steel under gas–liquid two-phase (CO₂/ aqueous solution) bubble flow conditions decreased obviously at the initial stage, then increased quickly, and then decreased gradually. Under the conditions of P_{CO2} = 0.1 MPa, V_L = 0.72 m/s, and V_g = 0.36 m/s, the corrosion rate reached the minimum value of 0.5504 mm/a at 3 h and the peak value of 2.6759 mm/a at 5 h.

2. The morphology characteristic of the corroded surface showed that the needle flocculent corrosion products formed preferentially at the area with defects such as
scratches, their crosses, or inclusion on the pipe wall, and then the corrosion products gradually extended around centering on the initial corrosion products. With the extension of the corrosion time, the corrosion products gradually became dense, and the inner corrosion product layer with a dual-structure characteristic formed, while the outermost corrosion product layer composed of spherical granular products formed at the same time. During the forming and densifying process of the outer corrosion product layer, the inner corrosion product layer with a dual-structure characteristic gradually differentiated into a dense underlying sub-layer with a columnar structure and a relatively dense middle sub-layer. The corrosion process far from the defect area lagged behind the defect area, but the evolution process and characteristic of the corrosion products were the same for the two kinds of areas.

(3) The main elements of the corrosion product layer were Fe, C, and O, and the main constituent phases were FeC, FeCO$_3$, FeOOH, Fe$_3$O$_4$, and FeO. The elemental analysis results showed that the Fe content of the inner layer of corrosion products was higher than that of the outer layer of corrosion products, while the content of C and O was just opposite to that of Fe. With the extension of the corrosion time, the Fe content in the corrosion product layer decreased gradually, while the contents of C and O increased accordingly.

**Author Contributions:** Conceptualization, G.Y. and W.S.; methodology, W.S.; software, Z.P.; validation, Z.P.; formal analysis, G.Y. and W.S.; investigation, G.Y. and W.S.; resources, W.S.; data curation, Y.M.; writing—original draft preparation, Z.P.; writing—review and editing, G.Y.; visualization, Y.M.; supervision, Y.H.; project administration, Y.M.; funding acquisition, Y.H. All authors have read and agreed to the published version of the manuscript.

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**Reference**


