

Impact of Flow on the Development of Iron Sulfide and Iron Carbonate Layers

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Received: February 02, 2023; Revised: May 15, 2023; Accepted: July 03, 2023

Flow is central to the operation of wells and pipelines and can be postulated to govern the formation of protective corrosion product layers, which is critical to overall infrastructure integrity. However, the phenomena involved remain poorly understood. Therefore, the main objective of this work was to investigate the effect of flow on the heterogeneous precipitation of FeS and FeCO₃ as corrosion products on mild steel. Initial corrosion studies were conducted in an autoclave stirred by an impeller. The tests were conducted under quiescent and dynamic conditions for 24 h in an aqueous brine (10 wt.% NaCl, 120°C, 5 bar CO₂, 0 and 10⁻³ mol/l Na₂S₂O₃). The experimental results showed that the increase in rotation speed did not prevent the formation of FeS or FeCO₃ crystals. Having confirmed the presence of corrosion product layers, the differences in the trends in corrosion rates may result from the diffusion barrier presented by these layers.

Keywords: Carbon steel; CO₂; EIS; SEM; XRD; high-temperature corrosion.

1. Introduction

The damage caused by different corrosive mechanisms is a challenge faced by the oil and gas industry. In this scenario, pipeline transmission is the most prevalent method of transporting production fluids due to its economic and structural advantages^{1,2}. According to a report by the American Petroleum Institute and the Association of Oil Pipelines, 229,454 miles of pipeline across America transport products from production sites to refineries and the consumer³. Most pipelines are made of carbon steel because of its economic advantages over other materials. Despite their excellent mechanical properties, carbon steels are prone to corrosion problems when exposed to an aqueous environment^{4,5}.

Corrosion mitigation remains challenging due to the operating conditions (temperature and pressure) and the contaminants in the transported fluids, such as CO₂, H₂S, organic acids, and salts^{6,7}. Currently, CO₂ injection techniques are widely used to improve oil recovery. In addition, carbon capture and storage (CCS) techniques have gained prominence as an effective technology to reduce carbon dioxide emissions and global warming⁸.

The effect of flow on the corrosive process has been a widely discussed topic in the literature¹⁻⁵. The contribution of flow to the corrosion phenomenon is associated with two main factors, mass transfer⁶⁻⁹, and wall shear stress¹⁰⁻¹².

In conditions where the formation of corrosion products with protective characteristics is not thermodynamically

stable (generally at low temperatures and pH), the effect of increasing fluid velocity is very evident¹³. Under these conditions, higher speeds mean an increase in the mass transfer of electroactive species to the steel surface, thus accelerating the corrosive process. The flow effect also gains prominence in conditions favorable to forming corrosion products, such as layers of iron carbonate in sweet conditions (CO₂) and layers of iron sulfide in acidic conditions (H₂S)¹⁴⁻¹⁶. The diffusion of iron ions (Fe²⁺) away from the steel surface increases with flow velocity, reducing saturation and limiting precipitation, which favors the formation of corrosion products with porous and non-compacted characteristics^{8,10}. Another flow effect discussed in the literature is the mechanical action of the hydrodynamic shear stress on the wall^{11,12}. However, commonly observed wall shear stresses in multiphase pipelines (1 Pa- 1kPa) are several orders of magnitude lower than the adhesion strength values of corrosion product layers (1 - 100 MPa)¹³⁻¹⁵. Thus, it is doubtful that multiphase flow can mechanically remove a dense and compact corrosion product layer.

Although the flow impact on the removal of corrosion products has been already understood as unlikely, its effect on the development of uneven and unprotective corrosion products layer remains unclear. Therefore, this work seeks to improve understanding of the flow impact on the precipitation of protective iron carbonate and iron sulfide layers on API 5L X65 carbon steel, through comparison between quiescent and dynamic aqueous brine conditions at 120°C.

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2. Experimental Procedure

The experimental system, shown in Figure 1, consists of a 2L 316L stainless steel autoclave with a 45° pitched blade impeller in the center to achieve controlled flow conditions. The purpose of conducting flow tests using an impeller to generate flow with static test specimens, rather than a rotating cylinder electrode (RCE), is to avoid the effects of centrifugal forces, which can mechanically affect the formation of corrosion product layers. At the same time, different samples can be used, ensuring that each sample is exposed to well-controlled and properly characterized mass transfer and shear stress conditions. A conventional three-electrode configuration was used to perform electrochemical measurements. Carbon steel specimens were machined from API 5L X65 (X65) carbon steel with a ferritic-pearlitic microstructure with the specified elemental composition provided in Table 1. A cylindrical API 5L X65 carbon steel specimen was used as a counter electrode and a cylindrical Hastelloy specimen was used as a reference electrode. In these experiments, two flat metal test specimens with an exposed area of 3.46 cm² located at the average height of the impeller blade were used, one for surface characterization and weight loss (WL) measurements (as described by an ASTM G1-03 procedure)¹⁷, and the second was used as a working electrode in electrochemical measurements. The bulk pH of the solution at room temperature was predicted

by water chemistry calculations considering test conditions and the addition of 0.3 g of NaHCO₃, resulting in an initial pH at 120 °C equal to 5.0. Although initial conditions were well controlled, once the autoclave was closed, there was no control of operating parameters beyond temperature and total pressure. The pH was not monitored during the test nor adjusted.

Each 24-hour experiment was conducted at a constant flow rate. Experiments were performed at quiescent speed and 1000 rpm of the impeller to evaluate the effect of flow on the formation of a protective layer of corrosion products under a slightly acidic (H₂S <10 ppm) and sweet environment. To facilitate comparison, equivalent fluid velocities were computed for a theoretical pipe with a diameter of 0.1 meters. It should be noted that these velocities are not simply derived from converting units from rpm to m/s. Rather, this calculation was performed by determining the mass transfer coefficient of H⁺ ions in the glass cell setup and finding the corresponding fluid velocity in a pipe using the established Sherwood correlation, which would produce the same mass transfer conditions^{7,18,19}. By doing this, mass transfer properties are combined. The hydrodynamic behavior of the system and the wall shear stresses on the steel surface were determined via computational fluid dynamics simulations. Table 2 summarizes the experimental parameters.

Environment conditions (T=120°C, 5 bar of CO₂) were selected to promote favorable conditions for the precipitation of protective corrosion products^{1,4,7,17,18}.

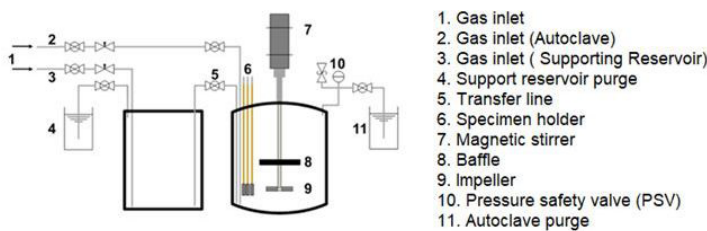


Figure 1. Autoclave setup.

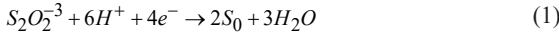
Table 1. Composition (wt.%) of API 5L X65 carbon steel.

Element	C	Mn	P	S	Si	Ni	Cr	Mo
	0.09	1.45	0.0.13	0.002	0.27	0.01	0.08	0.07

Table 2. Test matrix.

Parameter	Value
NaCl	10 wt. %
Na ₂ S ₂ O ₃	10 ⁻³ mol/L, and 0
H ₂ S	ca. 6 ppm, ca. 0 ppm
pH	5.0
Temperature	120°C
Total pressure	5 bars
Sparging gas	CO ₂
Impeller rotational speeds	0, and 1000 rpm
Equivalent Pipeline Velocity in 10 in pipe	0, and 0.6 m/s (1000 rpm)
Wall Shear Stress	0, and 6.7 Pa (1000 rpm)

Considering the toxicity of hydrogen sulfide (H_2S), some authors investigated sodium thiosulfate ($Na_2S_2O_3$) in corrosion experiments to simulate a marginally sour environment (<15 ppm) replacing the use of H_2S directly^{4,7,18,19}. They found that the compound dissociates, releasing thiosulfate ion ($S_2O_3^{2-}$) that is known to be reduced in acid brines generating H_2S , according to the following reactions²⁰.



According to the authors, the activation energy for the equations matches the corrosion potential of carbon steel in acidic media, making them spontaneous. The works mentioned above concluded that the concentration of 10^{-3} mol/L of sodium thiosulfate is sufficient to emulate a marginally sour medium that would lead to the precipitation of iron sulfide corrosion products on the metal surface. Then, the concentration of 10^{-3} mol/L of sodium thiosulfate ($Na_2S_2O_3$) was added to the solution to generate a sour environment. The H_2S concentration was measured *via* titration, and the value obtained was around 6 ppm.

The following experimental procedures were executed repeatedly in all the experiments. Before each experiment, the mild steel specimen was polished with 120-grit silicon carbide abrasive papers, then rinsed with distilled water, dehydrated with acetone, and air-dried before each experiment. The samples were placed inside the autoclave (Figure 1). The solution was stored in the supporting reservoir cell, and the system was closed. The solution was sparged with CO_2 for 2 h to remove oxygen and ensure the saturation of carbonic species in the solution. After the sparging period, the pre-heated solution was transferred from the supporting reservoir cell to the autoclave by pressure difference. When the test temperature was reached, the autoclave was pressurized with CO_2 to achieve 5 bars, and the impeller was turned on at the selected rotation speed.

An AUTOLAB μ Autolab type III/FRA2 potentiostat* was used for electrochemical and potential measurements. Open-circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and linear polarization resistance (LPR) measurements were taken. The EIS data were collected from 10 mHz to 10 kHz with 7 points per decade with a perturbation of 10 mV rms. The working electrode was polarized every 1 h during the experiments from -15 mV to +15 mV vs. the open-circuit potential, with a scan rate of 0.33 mV/s for linear polarization resistance (LPR) measurements. Corrosion rate from LPR were calculated using a B value equal to 26 mV²⁰. Potentiodynamic polarization curves were recorded at the end of each test.

After each experiment, the autoclave was depressurized, and the solution was cooled to approximately 50°C. The corroded specimens were retrieved, immediately rinsed with distilled water and acetone, dried with cool air, and stored in a vacuum desiccator to prevent any undesired oxidant of the corrosion products formed. A HITACHI TM3000† SEM was used to characterize the surface morphology of all specimens. The composition of the corrosion product layers was analyzed using XRD (Shimadzu XRS-600‡ from 10 to 85 2 θ).

The weight loss flat specimen was weighed after the experiment (with the corrosion product layer). After completion of surface characterization, the flat specimen was immersed in Clarke solution to remove the corrosion product layers, following recommendations of ASTM G1 standard¹⁶. The weight loss corrosion rates were calculated according to the equation described in the ASTM G31 standard²¹:

$$Corrosion\ rate = \frac{(K \times W)}{(A \times T \times D)} \quad (3)$$

Where K is a constant equal to 8.76×10^4 , W is the weight loss in grams, A is the specimen exposed area in cm^2 , T is the exposure time in hours, and D is the specimen density equal to $7.87\ g/cm^3$.

3. Results and Discussions

3.1. Marginally sour environment

3.1.1. Corrosion rates

Figure 2 shows the evolution of the corrosion rate over time for both quiescent and dynamic conditions. In the quiescent condition, rates started around 4 mm/y and then gradually decreased to reach 1.15 mm/y after 24 hours of the test. This decrease in corrosion rates is expected due to the likelihood for the formation of corrosion products under this condition^{1,4,18}. On the other hand, the dynamic flow condition showed at least twice the corrosion rate compared to the quiescent condition in the first measurement. Corrosion rates at 1000 rpm increased markedly overtime, reaching a peak at 5 hours into the test. However, in the following hours of the test, the corrosion rate dropped significantly, reaching values as low as 3.4 mm/y at 24 h of experimentation. Although precipitation of compact, dense, protective corrosion products is unlikely in most flow regimes, it has been reported that even under some level of wall shear stress, precipitation of protective layers can be expected^{8,17,22}.

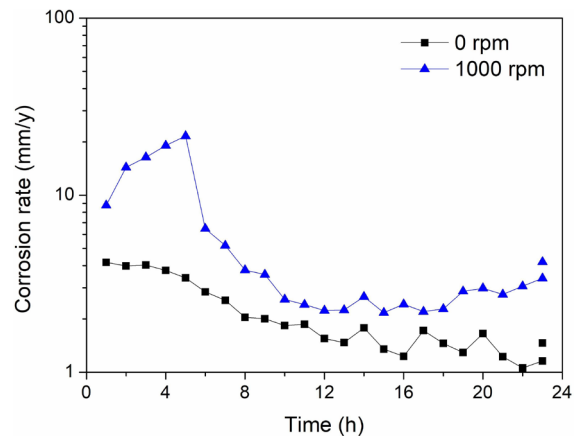


Figure 2. Comparison of LPR corrosion rates over time of X65 carbon steel for conditions at 0, and 1000 rpm, and WL corrosion rates. Condition: 10 wt. % NaCl, 10^{-3} mol/L of $Na_2S_2O_3$, initial bulk pH 5.0, 120°C, 5 bar CO_2 .

* Trade name

† Trade name

‡ Trade name

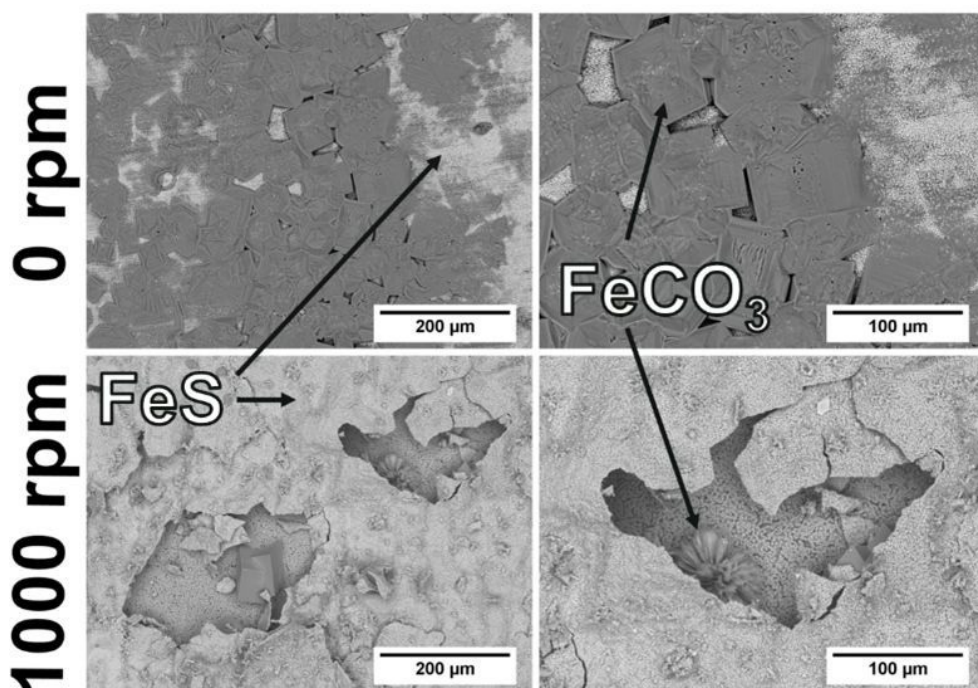


Figure 3. SEM magnifications of X65 carbon steel samples after tests at 0, and 1000 rpm. Condition: 10 wt. % NaCl, 10^{-3} mol/L of $\text{Na}_2\text{S}_2\text{O}_3$, initial bulk pH 5.0, 120°C , 5 bar CO_2 .

Once the flow increases the dissolution rate of the steel, local supersaturation of Fe^{2+} may occur, favoring the formation of corrosion products. Consequently, after a peak of high substrate dissolution (4-6 hours of the test), protective scales formed on the surface reducing corrosive activity and decreasing corrosion rates.

The weight loss measurement obtained after removing the corrosion products formed on the specimen surface showed that the corrosion rate at quiescent regime was approximately 3 times lower than the corrosion rate observed for the dynamic condition. The weight loss corrosion rate is more reliable and preferred in conditions with corrosion product formation since the surface kinetics could change with the surface condition. In these conditions, the LPR corrosion rate only gives, at best, a trend, and caution should be taken in interpreting the data.

3.1.2. Surface morphologies and characterization

Figure 3 shows that a dense corrosion product layer was formed under all tested conditions. At 0 rpm, FeCO_3 crystals were developed and distributed on the surface with some FeS structures. As shown in Figure 4, the corrosion product formed under quiescent conditions was identified as siderite (FeCO_3), which is the most developed iron carbonate product¹⁴. The presence of siderite crystals on the surface of the samples after testing in quiescent conditions is evident when analyzing the SEM images in Figure 3. In most field applications in the oil and gas industry, the presence of H_2S usually occurs simultaneously with the presence of CO_2 . Several studies seek to understand the interaction between these two mechanisms²¹⁻²⁷. Under quiescent conditions, in addition to the formation of developed siderite crystals,

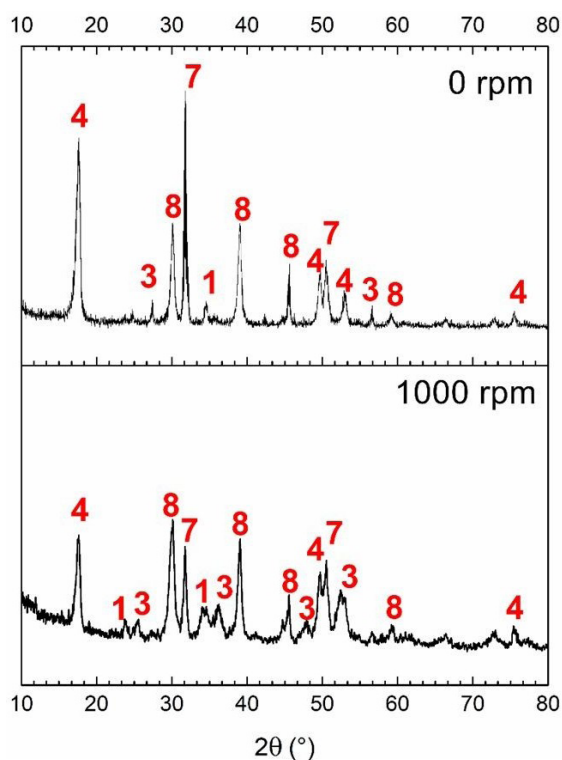


Figure 4. XRD spectra of X65 carbon steel for conditions at 0, and 1000 rpm in 10 wt. % NaCl, 10^{-3} mol/L of $\text{Na}_2\text{S}_2\text{O}_3$, initial bulk pH 5.0, 120°C , 5 bar CO_2 . 1. Chukanovite ($\text{Fe}_2(\text{OH})_2\text{CO}_3$), 2. Ferrite ($\text{Fe}-\alpha$), 3. Greigite (Fe_3S_4), 4. Mackinawite (FeS), 5. Magnetite (Fe_3O_4), 6. Pyrrhotite (Fe_{1-x}S), 7. Siderite (FeCO_3), 8. Smythite ($\text{Fe}_{3+x}\text{S}_4$), 9. Troilite (FeS).

a significant amount of iron sulfide phases was identified by XRD analysis, including mackinawite (FeS), smythite ($\text{Fe}_{3+x}\text{S}_4$) and greigite (Fe_3S_4). Some studies reveal that a porous layer of mackinawite can initially form on the steel surface and is easily broken²⁷. When more ferrous ions are released into the solution, more developed iron sulfide phases can precipitate on the steel surface due to high local supersaturation of iron sulfide. Variations in the morphology and crystalline structure of corrosion products interfere with their protective capacity or with the induction of new corrosive processes. In environments with low concentrations of H_2S such as the solutions in this study, literature shows that mackinawite is the main corrosion product formed and this initial layer, despite reducing corrosion rate values, does not have the capacity to stop the corrosive mechanism²⁸⁻³⁰.

Under dynamic conditions, similar structures of iron sulfide and iron carbonate were identified in the XRD analysis shown in Figure 4. However, the micrographic analysis of the film formed on the carbon steel surface obtained by SEM revealed significant differences. The formation of the mackinawite scale was the dominant process under dynamic conditions, while chukanovite and siderite crystals were mainly observed in regions where the mackinawite film had pores or cracks. There are no expressions in the literature to quantify the kinetics of mixed iron carbonate/sulfide scale formation in $\text{CO}_2/\text{H}_2\text{S}$ solutions. The composition of the corrosion product layer formed under these conditions depends on various factors, including not only the chemical composition of the medium and the respective solubility of

iron carbonate/sulfide but also on the competitive kinetics of the two mechanisms of corrosion product formation²⁵⁻²⁷. This difference in the development of iron sulfide and iron carbonate in carbon steel was expected based on the fact that the precipitation kinetics of iron sulfide layers are faster than those of iron carbonate layers. Therefore, in media with the presence of H_2S , mackinawite layers always form as the first layer on the steel surface, and iron carbonate crystals may precipitate in the external mackinawite scale, as shown in Figure 3^{25,27}. The formation of different phases of iron carbonate, i.e., siderite and chukanovite, under the test conditions described in this study is feasible³¹, suggesting that the intermediate metastable phase chukanovite transforms into a more stable phase of iron carbonate, siderite³². In addition to the influence of pH change on the crystallization rate of iron carbonate crystals, variations in the mass transport rate induced by the imposed flow are also known to interfere with the development and stability of the formed crystals³³. However, it was not possible to distinguish and, therefore, conclude whether the differences in observed morphologies were the result of the imposed flow or the competitive CO_2 and H_2S process.

3.1.3. Electrochemical measurements

To understand the effect of the flow on the FeCO_3 and FeS development on X65 carbon steel, EIS measurements were performed. Figure 5 shows the changes in the EIS spectra for an X65 carbon steel surface exposed to a CO_2 -saturated solution at quiescent and dynamic conditions at conditions of 10 wt. % NaCl, 10^{-3} mol/L of $\text{Na}_2\text{S}_2\text{O}_3$, initial bulk pH 5.0, 120°C, 5 bar CO_2 throughout the immersion time.

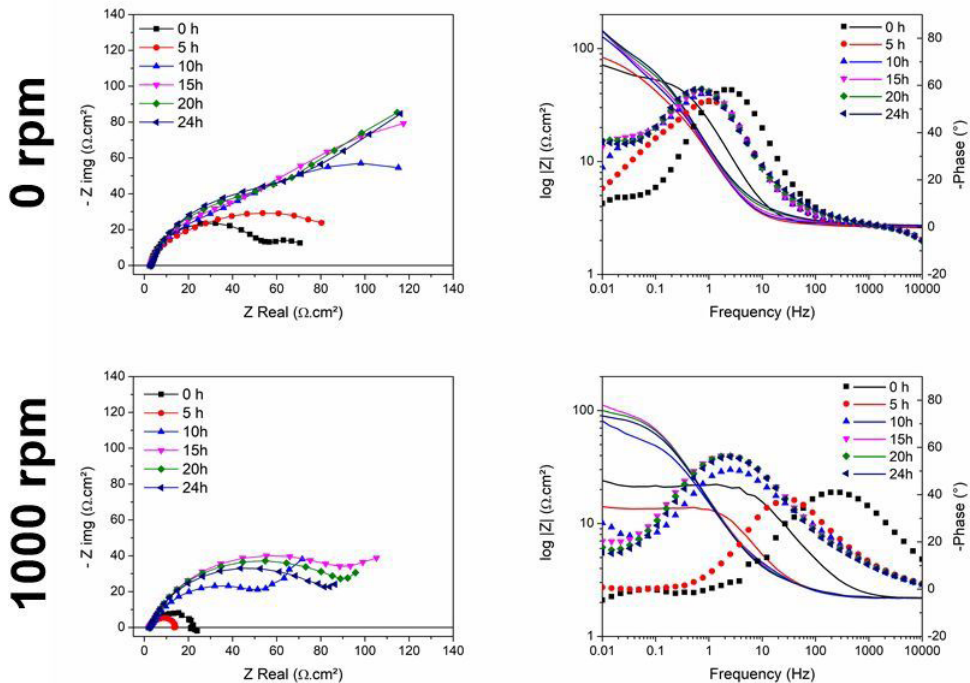


Figure 5. Nyquist diagrams and corresponding Bode diagram (modulus line plot, phase dot plot) of X65 carbon steel for conditions at 0 rpm and 1000 rpm, in 10 wt. % NaCl, 10^{-3} mol/L of $\text{Na}_2\text{S}_2\text{O}_3$, initial bulk pH 5.0, 120°C, 5 bar CO_2 .

A characteristic change in the capacitive trend in low frequencies as a function of time was observed in the shape of Nyquist plots, similar to that observed in the study by Souza et al.²³. Under both conditions (quiescent and 1000 rpm), the processes occurring at the metal surface change from charge transfer control (semi-circle) to diffusion or mass transfer control (45° straight line). The Bode modulus and phase angle corroborate the behavior observed. It was possible to notice that the Z module presented an increase with immersion time for both conditions. This behavior indicates the development of a protective corrosion product once the diffusion of the electroactive species (H^+) on the surface is retarded, reducing the corrosive process. Even though the condition under the dynamic regime did present a relatively low corrosion rate after 24 h (Figure 2), the corrosion product layer formed on the surface could not promote a greater capacitive character as observed under the quiescent regime. This assumption agrees with previous works that have found the same characteristics for mixed and porous coverage played by corrosion products^{13,23}.

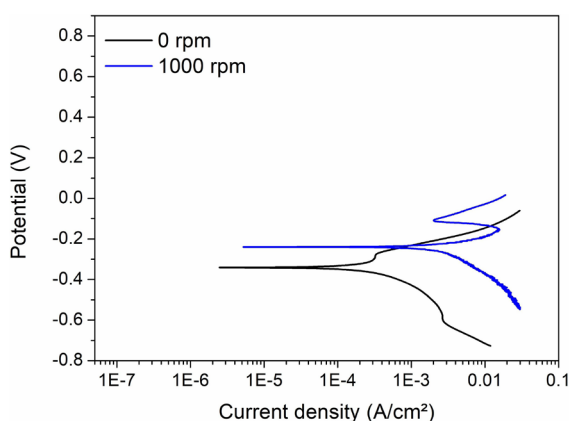


Figure 6. Polarization sweep curve, measured using a sweep rate of $0.033 \text{ mV} \cdot \text{s}^{-1}$, on X65 carbon steel, in 10 wt. % NaCl, 10^{-3} mol/L of $\text{Na}_2\text{S}_2\text{O}_3$, initial bulk pH 5.0, 120°C , 5 bar CO_2 at 0 rpm and 1000 rpm.

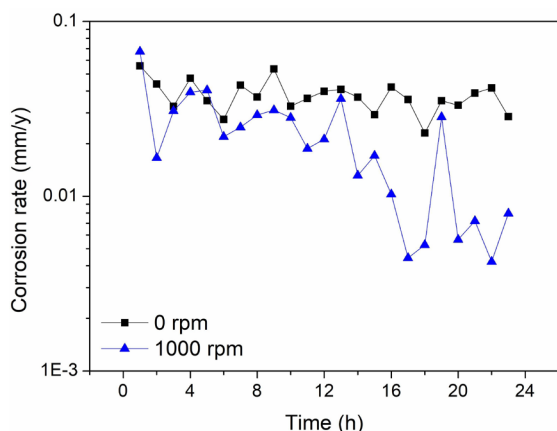


Figure 6 shows that the flow significantly increased the limiting currents for the dynamic conditions, as expected once the presence of flow affects the mass transfer region²⁴⁻²⁶. At 0 rpm, the anodic site showed the transition region, but no passivation character was observed in the range assessed. Therefore, even though the corrosion rates and the EIS data (Figure 5) showed that a film was formed at quiescent, no passive aspect was seen. On the other hand, for the dynamic condition, a passive trend is noticed. This passivation behavior is highlighted by the inflection on the anodic sweep that, at a certain point, the current density is abruptly reduced²⁷. Later, the current density decrease stops at the pitting potential and starts increasing again. Although the flow acted to increase the limiting currents on the cathodic site, the acceleration of the substrate dissolution due to flow might have led to changes in the local pH and consequently favored the precipitation of corrosion products that ended up being responsible for retarding electrochemical activity on the anodic sites^{28,29}. The increase in potential observed for conditions at the flow regime evidenced this behavior.

3.2. Sweet environment

3.2.1. Corrosion rates

Figure 7 shows the corrosion rate evolution over time for the quiescent and dynamic conditions (10 wt. % NaCl, initial bulk pH 5.0, 120°C , 5 bar CO_2) and compares the corrosion rate measured by using LPR and weight loss measurements after the removal of the corrosion products. Under the quiescent condition, the corrosion rate measured by using LPR started at 0.05 mm/y and gradually decreased to 0.028 mm/y after 24 hours of the test. This reduction in the corrosion rate is associated in the literature with the precipitation of corrosion products^{13,23,30}. The formation of iron carbonate during the test was confirmed by comparing the corrosion rate values obtained by weight loss of 3.23 mm/y with the values obtained by the LPR measurements.

When plotting the LPR corrosion rate measurements, it was noted that the initial corrosion rate increased for the dynamic condition but reached lower values after 24 hours of immersion under the test condition.

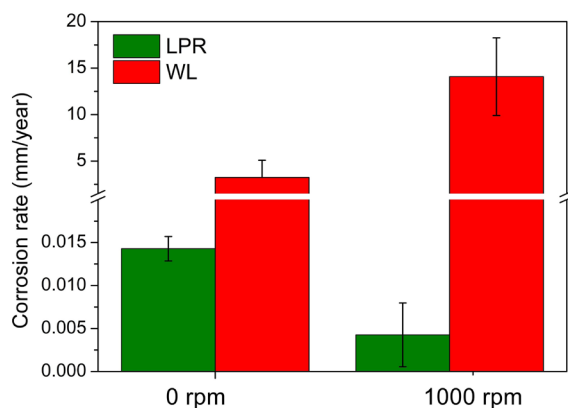


Figure 7. Comparison of LPR corrosion rates over time of X65 carbon steel for conditions at 0 and 1000 rpm and WL corrosion rates. Condition: 10 wt. % NaCl, initial bulk pH 5.0, 120°C , 5 bar CO_2 .

The corrosion rate obtained by LPR measurements for the dynamic condition was approximately four times lower than that observed in the static condition. In comparison, the corrosion rate obtained by weight loss was four times higher. This discrepancy between the corrosion rate values obtained by different methodologies is postulated to be related either by the uncertainty of the B value used or because LPR cannot precisely account the change in surface area for the cathodic reaction^{9,31,32}. The increase in the corrosion rate due to mass loss indicates consumption of the metallic substrate during the immersion period, releasing Fe^{2+} ions. The increase of dissolved Fe^{2+} in the medium, the increase in rotational speed, and high temperatures promote a more significant transport of ionic species, promoting nucleation and precipitation of a protective FeCO_3 film, resulting in a lower value for the corrosion rate observed in electrochemical measurements^{18,31}.

3.2.2. Surface morphologies and characterization

Figure 8 shows the SEM images of the surface of the specimen for 0 rpm and 1000 rpm experiments after 24 h immersion time. The dense and compact formation of FeCO_3 crystals observed on the entire surface of samples justifies the good electrochemical behavior under both conditions^{1,4,18}. At 0 rpm, a homogeneous formation of FeCO_3 crystals can be observed (Figure 8) with a predominance of the most developed iron carbonate structure (siderite), as shown in the XRD spectra in Figure 9. The specimen for the 1000 rpm experiment shows a surface covered by prismatic FeCO_3 crystals, which are a protective layer as indicated by the decrease of corrosion rate to a low value as shown in Figure 7^{4,9,33}. According to the literature, the higher the flow velocity in the medium the more complex is the formation of

a corrosion product layer due to heterogenous distribution of wall shear stress on the surface³¹. However, it was possible to verify a dense appearance of FeCO_3 on the sample surface.

Furthermore, the XDR analysis confirmed that the corrosion product formed was the siderite phase, the most stable FeCO_3 phase. The SEM images explain the corrosion rate results obtained for the sample tested at 1000 rpm. The increase in rotational speed promoted a more accelerated corrosive process^{9,34,35} which at the temperature and in the test medium, enabled a combination between the consumption of metallic substrate and the formation of corrosion products. This process resulted in high weight loss corrosion rates. At the same time, the rapid formation of FeCO_3 reduced the anodic and cathodic reactions on the sample surface, resulting in lower LPR corrosion rates.

3.2.3. Electrochemical measurements

While corrosion rate measurements illustrate the evolution of steel surface dissolution under controlled flow conditions in a CO_2 environment, impedance measurements provide information about the corrosion mechanisms at the interface. Figure 10 shows the evolution of the EIS data throughout the 24 hours of the experiment for each condition. The Nyquist representation shows two loops with different amplitudes, though they seem linear. The first semi-circle can be observed at high frequencies, and in low and medium frequencies, a second loop where high amplitude is evident. The Bode modulus (Figure 10 – line plot) and phase (Figure 10 – dot plot) corroborate with the presence of the two responses. The former illustrates that under quiescent conditions, the maximum point remains relatively constant in the medium and high frequencies, while the maximum point increases with time at low frequencies.

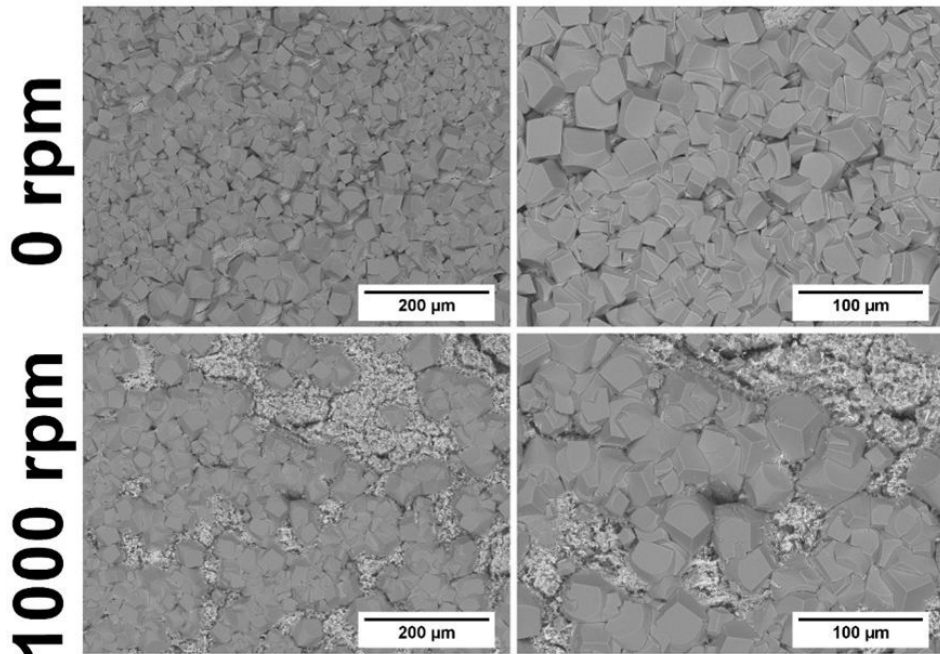


Figure 8. SEM magnifications of X65 carbon steel samples after tests at 0 and 1000 rpm. Condition: 10 wt. % NaCl, initial bulk pH 5.0, 120°C, 5 bar CO_2 .

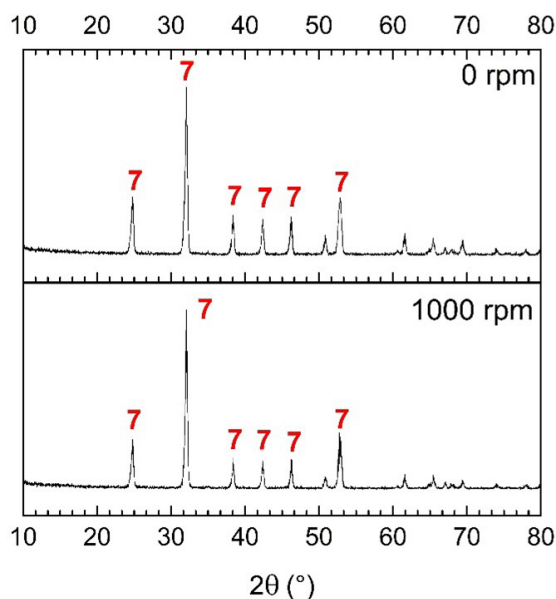
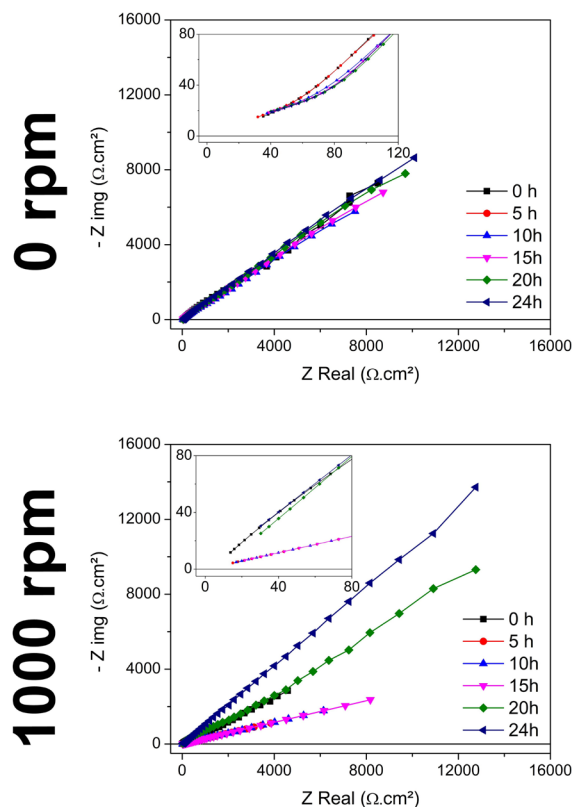


Figure 9. XRD spectra of X65 carbon steel for conditions at 0 and 1000 rpm in 10 wt. % NaCl, initial bulk pH 5.0, 120°C, 5 bar CO₂. 1. Chukanovite (Fe₃(OH)₂CO₃), 2. Ferrite (Fe-α), 3. Greigite (Fe₃S₄), 4. Mackinawite (FeS), 5. Magnetite (Fe₃O₄), 6. Pyrrhotite (Fe_{1-x}S), 7. Siderite (FeCO₃), 8. Smythite (Fe_{3+x}S₄), 9. Troilite (FeS).



For the dynamic condition, it was possible to observe an increase in impedance modulus with the time at all frequency ranges. The behavior observed for both conditions was attributed to the continuous precipitation of FeCO₃, which increases the charge transfer resistance due to the cathodic reaction by blocking charge transfer sites¹³. Another critical behavior to highlight is the influence of the flow on the electrochemical response in EIS experiments. It was possible to notice that the increase in the velocity from 0 to 1000 rpm led to a notable increase in the diameter of the capacitive loops. Even with the less compact formation of a FeCO₃ layer, at the dynamic condition, the transport of ionic species promoted fast nucleation of a protective FeCO₃ film³¹, resulting in a more protective electrochemical response, as shown in Figure 7 and Figure 10.

The potentiodynamic polarization test for each condition was carried out, as shown in Figure 11. The curves showed that the measured cathodic current is affected by the flow. The current can be associated with the diffusion of H⁺ ions from the bulk solution to the surface of the electrode, where they reduce to H₂ gas³⁶. This behavior can also demonstrate that the flow dependency of the i_{lim} can be associated with the diffusion process. For both conditions, a passive trend was noted in the anodic region. A FeCO₃ layer can promote mild steel passivation, and this passivation process can be achieved when the iron carbonate saturation point is greater than unity²⁷.

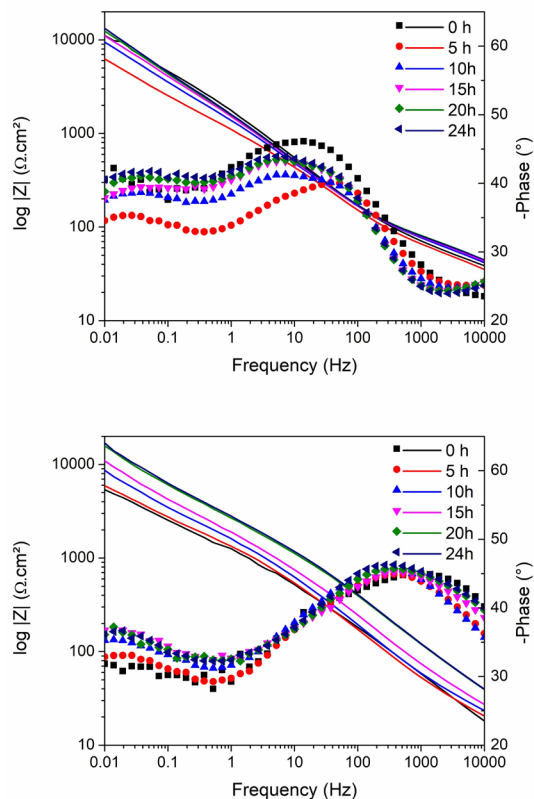
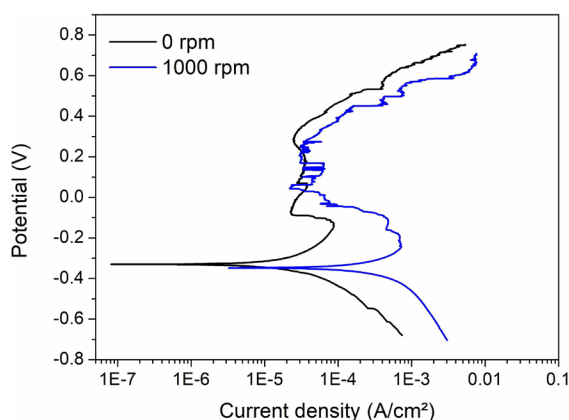


Figure 10. Nyquist diagrams and corresponding Bode diagram of X65 carbon steel for conditions at 0 rpm and 1000 rpm, in 10 wt. % NaCl, initial bulk pH 5.0, 120°C, 5 bar CO₂.

Table 3. Comparison of the final corrosion rate (LPR and WL) and the corrosion product precipitation.

Condition	Final LPR Corrosion Rate (mm/year)		WL Corrosion Rate (mm/year)		Corrosion product precipitation	
	0 rpm	1000 rpm	0 rpm	1000 rpm	0 rpm	1000 rpm
With $\text{Na}_2\text{S}_2\text{O}_3$	1.15	3.36	1.46	5.10	Dense FeCO_3 with some FeS structures	Dense and brittle FeS with few FeCO_3 crystals
Without $\text{Na}_2\text{S}_2\text{O}_3$	0.01	0.004	3.23	14.08	Dense and uniform FeCO_3	Dense FeCO_3

**Figure 11.** Polarization sweep curve, measured using a sweep rate of $0.033 \text{ mV} \cdot \text{s}^{-1}$, on X65 carbon steel, in 10 wt. % NaCl, initial bulk pH 5.0, 120°C , 5 bar CO_2 at 0 rpm and 1000 rpm.

As previously shown, a uniform layer of FeCO_3 was formed on the surface of the samples tested in CO_2 medium at 0 rpm and 1000 rpm, as shown in the SEM images (Figure 8).

4. Analysis

The flow in the system and the corrosive medium in which the carbon steel samples were immersed played a crucial role in the precipitation and development of FeS and FeCO_3 . It was verified that the flow did not prevent the formation of a dense layer of corrosion products such as FeS and FeCO_3 in the marginally sour environment. Despite the dense precipitation of corrosion products under the tested conditions, the flow may have prevented the development of a more stable iron carbonate structure. Corrosion rates obtained under dynamic conditions were about three times higher than the static condition in the sour medium. These results seem to coincide with what other researchers suggest being the formation of multilayer corrosion products where FeS covered FeCO_3 crystals^{13,18,23}.

The results obtained in the sweet experiment indicated a dense formation of FeCO_3 on the surface of the samples. Under these conditions, a significant discrepancy was observed between the corrosion rate values obtained by LPR and by weight loss. The imposition of the flow resulted in a less dense formation of iron carbonate compared to the static condition. The results indicated that even with the less compact formation, the transport of ionic species promoted the rapid nucleation of a FeCO_3 protective film in the dynamic condition³¹, which explains the electrochemical response observed in this work.

Table 3 compares findings for this set of experiments for all conditions tested, including the final corrosion rates obtained by LPR measurements and weight loss measurements after removing the corrosion products. The general description of the corrosion product observed at the end of the experiments.

5. Conclusions

Experimental studies were performed to assess the impact of fluid flow on the development of iron sulfide (FeS) and iron carbonate (FeCO_3) layers on the API X65 carbon steel. The specimens were tested in a 5 bar CO_2 with and without 10^{-3} sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to simulate the acidic environment and vary the impeller rotation velocity. Based on the outcome of this investigation, the following conclusions are made:

- Adding sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to the solution as an alternative to bubbling H_2S has been successfully used. The generated hydrogen sulfide concentrations were enough to simulate the acid corrosion mechanism.
- The increase in rotation speed did not prevent the formation of FeS or FeCO_3 crystals.
- The competitive effect between FeS and FeCO_3 crystals led to the formation of less stable phases.
- The differences in the trends in corrosion rates result from the different diffusion barriers presented by these layers of the dense and stable FeCO_3 crystals and the mixture of FeCO_3 and FeS.
- In the medium without $\text{Na}_2\text{S}_2\text{O}_3$, the dynamic condition resulted in lower corrosion rates due to an increase in the transport of ionic species.
- FeCO_3 -developed crystals had their precipitation favored at quiescent conditions.

6. Acknowledgements

The authors would like to thank the financial support of Federal University of São João del Rei (UFSJ), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil – Finance Code 001), CNPq (Brazilian National Council of Technological and Scientific Development - 405505/2021-3), and FAPEMIG (The Minas Gerais Research Funding Foundation – APQ-02540-21).

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