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Corrosion Behavior of S235JR Carbon Steel in 0.5 M HCl Solution During 24 Weeks

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Abstract

This study aims to evaluate the corrosion behavior of and morphological changes in S235JR steel exposed to 0.5 M hydrochloric acid solution over a period of 24 weeks. Corrosion resistance was assessed through weight loss measurements and electrochemical techniques (such as open circuit potential (OCP), polarization resistance (R_p), and corrosion rate (V_{corr})), while surface morphology, elemental analysis, roughness, and Vickers hardness were also analyzed. All evaluations were performed at the same immersion intervals: 2, 4, 8, 12, and 24 weeks. The corrosion rate started at 0.9 mm/year after the first hour of immersion, then decreased due to the formation of corrosion products on the steel surface, and fluctuated during prolonged exposure, reaching a maximum of 8.5 mm/year after 24 weeks. Weight loss increased gradually during the first 8 weeks, followed by a more pronounced rise. Polarization resistance and corrosion rate exhibited dynamic variations. SEM analysis revealed severe surface degradation, including cracks and deep pits. Surface roughness increased significantly from an initial value of 0.91 µm to 9.03 µm at 24 weeks. Vickers hardness dropped from 148.7 HV0.5 to 87.3 HV0.5, due to non-uniform corrosion product formation. These findings highlight the progressive deterioration of S235JR steel in acidic environments and provide valuable insight into its long-term corrosion resistance.

Keywords: carbon steel; corrosion; immersion time; acidic environments; surface characterization

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Academic Editor: Luis Cáceres

Received: 12 September 2025
Revised: 25 September 2025
Accepted: 29 September 2025
Published: 29 September 2025

Citation: Mureșan, A.C.; Buruiana, D.L.; Ghisman, V.; Herbei, E.E.; Bogatu, N. Corrosion Behavior of S235JR Carbon Steel in 0.5 M HCl Solution During 24 Weeks. *Metals* **2025**, *15*, 1092. https://doi.org/10.3390/met15101092

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1. Introduction

Carbon steels are widely utilized across various industrial sectors including construction, energy, and high-tech equipment manufacturing owing to their favorable mechanical properties, cost efficiency, affordability, and high tensile strength [1–3]. Despite these advantages, carbon steels are particularly susceptible to corrosion when exposed to aggressive environments containing chloride, sulfate, and nitrite ions, commonly encountered during industrial processes such as pickling, descaling, and acid stimulation in oil wells [4,5]. Corrosion significantly compromises structural integrity, leading to performance degradation, considerable economic losses, and potential safety hazards [6–9].

Among the various carbon steels, S235JR is frequently used in the oil and gas industry (e.g., for petroleum product storage tanks and pipelines) due to its good machinability, low production cost, and efficient processing capabilities [10–12]. However, S235JR steel demonstrates a notable vulnerability to electrochemical corrosion in acidic environments,

particularly when exposed to mineral acids such as hydrochloric and sulfuric acid (HCl and H_2SO_4) [13]. The formation of corrosion products and surface rust can drastically impair mechanical properties and shorten the operational lifespan of equipment.

A key parameter in evaluating corrosion behavior is the corrosion rate. Previous studies have focused primarily on the corrosion performance of S235JR steel under atmospheric conditions or during short-term immersion in acidic media [14–16]. These investigations have shown that corrosion progression in carbon steel is nonlinear and often fluctuates over time, attributed to passivation film formation and its subsequent breakdown.

Some studies have further revealed that in dynamic or turbulent environments, increased surface roughness and friction contribute to an increased corrosion rate as corrosion products accumulate [17,18].

Several studies have evaluated the corrosion behavior of S235 steel in hydrochloric acid solutions of varying concentrations (15%, 1 M, 0.1 M) over short immersion periods [19–26]. These works consistently indicate a high corrosion susceptibility of carbon steel in acidic media. For instance, Liao et al. reported a corrosion current density of 2.64×10^{-3} A/cm^2 after 24 h in 1 M HCl [19], while Fang et al. observed 1.395×10^{-3} A/cm^2 after 12 h [20]. Similarly, Peng et al. identified comparable corrosion behavior for Q235 steel in 0.1 M HCl [21], and Singh et al. recorded a corrosion rate of 39.68 mm/year after 12 h in 15% HCl [22]. Du et al. quantified a weight loss of 16.38 g·m^{-2}·h^{-1} after 24 h in 1 M HCl [23], and Huang et al. measured a corrosion current density of 3.029×10^{-3} A/cm^2 after 48 h, alongside temperature-dependent weight loss data [24,25]. Lu et al. reported a weight loss of 7.02 mm/year after 4 h of immersion [26].

While these contributions offer valuable insight, most are limited to short-term immersion and high acid concentrations, leaving a significant lack of understanding regarding the long-term corrosion behavior of S235JR steel immersed in 0.5 M HCl solution.

HCl is one of the most used acids in industrial applications, including chemical cleaning, oil refining processes and well acidification [27]. From a corrosion perspective, hydrochloric acid represents one of the most aggressive environments for steel and its alloys, requiring special attention in the choice of materials [27]. Moderate concentrations, such as 0.5 M, are encountered in industrial applications and are aggressive enough to cause active corrosion, but at the same time allow the evaluation of long-term phenomena. The choice of this concentration made it possible to investigate the corrosion evolution of carbon steel over 24 weeks, under practically relevant conditions, but without the accelerated surface damage that occurs at higher concentrations.

The present study addresses this research deficiency by investigating the long-term corrosion behavior of S235JR steel immersed in 0.5 M HCl solution over a 24-week period.

The novelty of the present study resides in the systematic long-term evaluation (up to 24 weeks) of the corrosion behavior of S235JR carbon steel in 0.5 M HCl solution, a condition insufficiently explored in the current literature. While most existing studies concentrate on short-term immersion durations and higher acid concentrations, this work provides a comprehensive analysis of the temporal evolution of electrochemical parameters (open circuit potential, polarization resistance, corrosion rate), along with detailed surface morphology, elemental analysis, roughness, and hardness characterizations at multiple exposure intervals. The extended immersion period enables a deeper understanding of the progressive degradation mechanisms that affect S235JR steel in acidic environments and contributes to bridging a major knowledge void in the field. Finally, this study aims to support the selection of appropriate operational conditions and materials to reduce corrosion-related costs and improve the durability of low-carbon steels in aggressive environments.

2. Materials and Methods

2.1. S235JR Carbon Steel

For this study was used S235JR carbon steel plates supplied by Mairon Galati, Romania with the chemical composition presented in Table 1.

Table 1. Chemical composition of carbon steel S235JR [wt.%]. Adapted from [9].

Mn	Si	P	S	N	Cu	C	Fe
≤1.40	≤0.025	≤0.028	≤0.025	≤0.012	≤0.45	≤0.17	Balance

For the gravimetric (weight loss) analysis, rectangular samples with an active surface area of 15 cm^2 ± 0.1 (dimensions 5 cm × 3 cm × 0.3 cm) were used, of which only one part was exposed to corrosion, while the remaining part was protected with resin. Electrochemical measurements were performed on samples with an exposed working area of 8 cm^2 ± 0.5, embedded in epoxy resin to ensure a well-defined surface. Prior to testing, all steel surfaces were mechanically abraded with silicon carbide papers of 600, 800, and 1200 grit, ultrasonically degreased in acetone, rinsed with deionized water, air-dried, and stored in a desiccator for 24 h to ensure surface stability and minimize environmental contamination.

2.2. Gravimetric Corrosion Measurements

Gravimetric measurements were performed on S235JR carbon steel samples with dimensions of 5 × 3 × 0.3 cm (15 cm^2 ± 0.1) prepared by mechanical polishing using progressively finer abrasive papers (up to P1200 grit), followed by degreasing with ethanol and air drying. The samples were then immersed in Berzelius glasses with a total volume of 500 mL, each containing 300 mL of 0.5 M HCl solution as the corrosive medium. The experiments were conducted at room temperature (22 °C ± 1 °C) under static, non-aerated conditions to simulate a quiescent system and to avoid the influence of dissolved oxygen on corrosion kinetics at different interval period measurements (2, 4, 8, 12 and 24 weeks).

After the predetermined exposure time, the samples were carefully removed, rinsed thoroughly with distilled water to remove acid residues, then cleaned from corrosion products (consisted of a light mechanical cleaning with filter paper followed by washing with absolute ethanol and drying with a high-purity nitrogen flow).

The experimental protocol followed the recommendations of ASTM G31—Standard Guide for Laboratory Immersion Corrosion Testing of Materials [28], and ISO 11845:2020 [29], which provide validated methods for testing and evaluating corrosion behavior in acidic aqueous solutions. The initial and final mass of each sample was measured using a high-precision analytical balance (Kern EWJ 300-3H, Kern & Sohn, Albstadt, Germany, with 0.001 g precision) to calculate mass loss.

Based on these measurements, both the relative weight loss (%) and corrosion rate expressed in mm/year were determined using the relations from ASTM G1-90 (1999) [30], as presented in Equations (1) and (2).

$$\text{Weight loss } (\%) = \frac{(W_1 - W_2)}{W_1} \cdot 100 \quad (1)$$

$$CR(\text{mm /year}) = \frac{(W_1 - W_2) \cdot K}{A \cdot t \cdot d} \quad (2)$$

where K is a constant dependent on the units employed for corrosion rate (in this case, 8.76×10^4), $(W_1 - W_2)$ denotes the mass loss calculated as the difference in weight of the steel samples before and after immersion (unit measurement g), A represents the total

surface area of the exposed metal samples (cm^2), (t is the exposure duration (hours), and d is the density of the metal substrate, taken as 7.87 g/cm^3 for iron.

The values of these parameters used in the calculations of Equations (1) and (2) are presented in Table 2.

Table 2. Values of parameters used for the calculation of mass loss and corrosion rate of S235JR steel during 24 weeks from immersion time.

Parameters	Period of Immersion [Weeks]				
	2 (After 2 Weeks)	**4 (After 4 Weeks)**	**8 (After 8 Weeks)**	**12 (After 12 Weeks)**	**24 (After 24 Weeks)**
W_1 [g]	34.9317 ± 0.002	34.5117 ± 0.005	35.0814 ± 0.002	34.9376 ± 0.005	35.0690 ± 0.002
W_2 [g]	32.8421 ± 0.003	32.3766 ± 0.007	32.9151 ± 0.004	32.5396 ± 0.003	32.4950 ± 0.006
A [cm^2]	15 ± 0.1				
t [h]	336	672	1344	2016	4032
K	87.600				
d [g/cm^3]	7.87				

Each experimental condition was assessed in triplicate, and the mean value of the three measurements was reported.

2.3. Electrochemical Measurements

The gravimetric technique is a standard approach for assessing the corrosion rate of metals in aggressive environments [31]. However, it is limited by the need for prolonged exposure durations and does not provide real-time insights into corrosion behavior. In contrast, electrochemical techniques offer rapid and precise measurements, making them highly valuable for practical applications.

Continuous monitoring of corrosion processes can be achieved through linear polarization, a method known for its short acquisition times and high sensitivity. Nevertheless, the application of an external potential can perturb the system, potentially altering its intrinsic electrochemical properties [32].

Electrochemical evaluations were carried out using a conventional three-electrode cell setup connected to a Voltamaster 4–PGP 201 system, interfaced with a computer running VoltaMaster software version 5.10. In this configuration, a platinum electrode served as the counter electrode, a saturated calomel electrode (SCE) was used as the reference, and the working electrode was a sample of S235JR carbon steel with an exposed geometric area of 8 ± 0.5 cm^2. Measurements were performed both at initial immersion and after various exposure periods (2, 4, 8, 12, and 24 weeks) in 250 mL of 0.5 M HCl solution at room temperature.

The physico-chemical parameters of the 0.5 M hydrochloric acid solution used as the corrosive medium were measured using a multiparameter analyzer (Phoenix Instrument, model multiEC-15, PHOENIX Instrument, Garbsen, Germany), and the obtained values are presented in Table 3.

To determine polarization resistance and corrosion rate at different exposure times, open circuit potential (OCP) monitoring was conducted for each specimen over a 60 min period, with data acquisition at intervals of approximately 0.6 s. A total of 40 data points were collected per measurement, using a scan rate of 1 mV/s, with an overpotential of 40 mV. The interval between each R_p and V_{corr} determination was set to 1 min. Each R_p—V_{corr} measurement sequence comprises 40 data points, each derived from individual linear polarization curves. The corrosion parameters were calculated based on the Stern—Geary

relationship, as expressed by Equations (3) and (4). All experiments were performed in triplicate for each sample type to ensure reproducibility and statistical relevance.

$$i_{cor} = \frac{B}{R_p} \quad (3)$$

$$B = \frac{b_a|b_c|}{2.303(b_a + |b_c|)} \quad (4)$$

where i_{cor} represents the corrosion current density, B is a constant characteristic of the electrochemical system, R_p denotes the polarization resistance, b_a is the anodic Tafel slope, and b_c corresponds to the cathodic Tafel slope.

Table 3. Physico-chemical parameters of 0.5 M HCl solution before and after corrosion.

Period of Immersion	pH	Electrical Conductivity [mS/cm]	Salinity [g/L]	TDS (Total Dissolved Solids) [ppt]
0 (initial)	0.53 ± 0.006	155.5 ± 4.2	102.0 ± 6.3	110.7 ± 2.8
2 (after 2 weeks)	3.35 ± 0.2	40.2 ± 0.9	25.0 ± 1.5	28.5 ± 1.2
4 (after 4 weeks)	3.50 ± 0.1	40.3 ± 1.3	25.0 ± 0.6	28.6 ± 2.3
8 (after 8 weeks)	4.13 ± 0.3	40.3 ± 0.5	25.1 ± 0.7	28.7 ± 3.2
12 (after 12 weeks)	3.21 ± 0.1	41.0 ± 2.6	25.6 ± 1.4	29.1 ± 0.9
24 (after 24 weeks)	3.14 ± 0.4	40.6 ± 1.8	25.2 ± 0.5	28.9 ± 1.3

2.4. Surface Analysis and Elemental Composition

Prior to immersion and following exposure periods of 2, 4, 8, 12, and 24 weeks in 0.5 M HCl solution, the steel samples were retrieved for analysis. The surface morphology and elemental analysis of the S235JR carbon steel was examined using a scanning electron microscope (EDS, Oxford Instruments, Abingdon, UK), SEM model TESCAN VEGA 3 LMH (TESCAN ORSAY HOLDING, Brno, Czech Republic). The SEM investigations were conducted at an accelerating voltage of 20 kV.

2.5. Roughness and Vickers Hardness Measurements

The surface roughness of the steel samples was accurately evaluated both before and after corrosion testing using an Insize ISR-C002 roughness tester (Insize Co., Suzhou, China). The analysis considered several roughness parameters, including Ra (arithmetical mean of the absolute values of the profile deviations from the mean line), Rz (mean roughness depth), Rq (root mean square roughness), and Rt (total height of the roughness profile), as defined in standards [9,31,32].

Vickers microhardness measurements were carried out before and during exposure to 0.5 M HCl using a Digital Micro-Vickers hardness tester (ISR-C100, Insize Co., Suzhou, China). A diamond pyramid-shaped indenter was applied with a constant load of 0.5 kg (approximately 4.9 N) on the upper surfaces of the tested samples.

All roughness and hardness values represent the average of three independent measurements taken for each steel specimen to ensure accuracy and reproducibility.

3. Results and Discussion

3.1. Weight Loss Results

The weight loss method is widely regarded as one of the most reliable and straightforward techniques for evaluating the corrosion rate of steels, due to its simplicity, reproducibility, and ability to reflect long-term degradation behavior [33]. The calculated corrosion parameters derived from the weight-loss data, such as corrosion rate (mm/year)

and mass loss (%), are presented in Figure 1 for S235JR steel exposed to 0.5 M HCl over a 24-week period at different immersion intervals (2, 4, 8, 12, and 24 weeks).

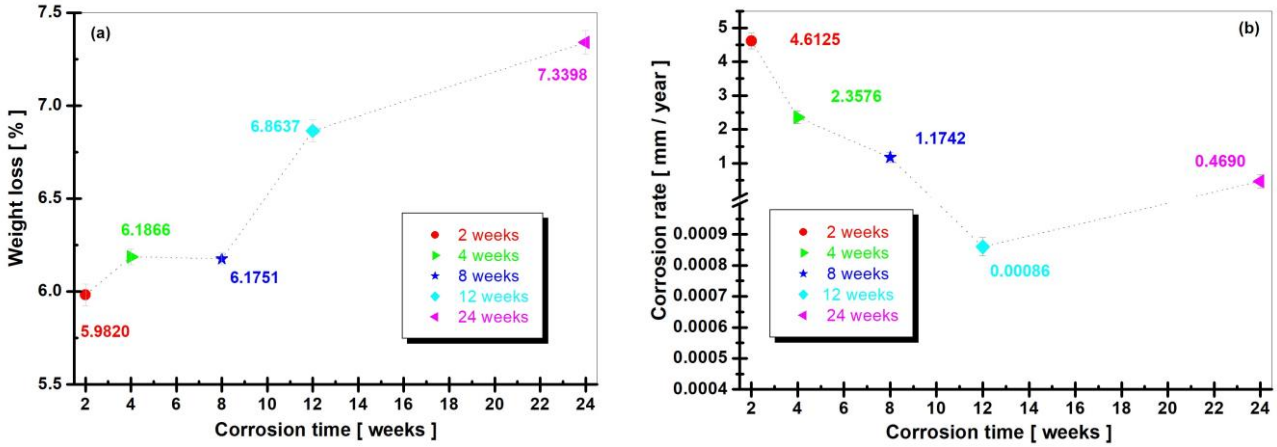


Figure 1. Weight loss (**a**) and corrosion rate (**b**) of S235JR tested samples after different time of immersion in 0.5 M HCl solution.

Immersion tests in 0.5 M HCl solution were conducted to investigate the long-term corrosion behavior of S235JR structural steel. As illustrated in Figure 1, the cumulative weight loss increases slowly over the first 8 weeks of immersion, indicating a relatively stable corrosion process during the initial phase. Beyond this period, weight loss becomes more pronounced, suggesting a potential shift in the corrosion mechanism or the breakdown of protective surface layers.

After 2 weeks of exposure, the corrosion rate is relatively high, reaching 2.3576 ± 0.18 mm/year, which is typical for active corrosion in an aggressive acidic environment.

This shift indicates a gradual neutralization of the acidic environment, likely due to the consumption of hydrogen ions during the cathodic reduction reaction and the accumulation of corrosion products such as Fe^{2+} and Fe^{3+} species, which can form oxides and chloride salts [34,35].

However, a significant decrease in the corrosion rate is observed at later intervals—4, 8, 12, and 24 weeks dropping to a final value of 0.4690 ± 0.023 mm/year. This marked reduction suggests the development of corrosion products, that gradually accumulate on the steel surface.

Corrosion products formed on steel surfaces can develop into a semi-protective layer that hinders the transport of aggressive species such as chloride and hydrogen ions to the steel surface, thereby slowing the active corrosion rate over time. While these layers are typically porous and uneven, they can nonetheless serve as physical barriers that restrict further metal dissolution in acidic environments [36,37].

The gravimetric analysis revealed a significant decrease in the corrosion rate of S235JR steel with prolonged immersion in 0.5 M HCl solution, dropping from 2.3576 ± 0.18 mm/year after 2 weeks to 0.4690 ± 0.023 mm/year after 24 weeks.

A similar behavior has been reported in the specialized literature, where other authors have investigated the corrosion process of carbon steel in hydrochloric acid solutions of varying concentrations, over extended time intervals 15 days [27], 360 h [34]. Saad et al. [27] investigated the corrosion behavior of carbon steel in 1, 2 and 3 M HCl solutions for 15 days and demonstrated that, despite the initially severe attack in highly acidic conditions, the corrosion rate decreased with immersion time. This reduction was attributed to the

progressive accumulation of corrosion products, which partially shield the metallic surface and modify the corrosion mechanism [27].

Fajobi et al. [34], in their study investigated the electrochemical response of austenitic 316L stainless steel and carbon steel through weight loss analysis during immersion in 1 M, 2 M, and 3 M HCl solutions for 360 h.

The authors reported that the corrosion process is initially governed by anodic dissolution of iron coupled with cathodic proton reduction, while with increasing exposure time the surface becomes progressively covered by corrosion products [34].

These corrosion products can act as semi-protective layers that reduce the electrochemically active surface area and hinder charge transfer, thereby decreasing the overall corrosion rate [34].

3.2. Electrochemical Measurement Results

3.2.1. OCP (Open Circuit Potential)

Before initiating further electrochemical experiments, it is essential to ensure that the system under investigation has reached electrochemical equilibrium, typically assessed through the stabilization of the open circuit potential (OCP) [38]. A stable OCP indicates the establishment of a steady-state condition, which is crucial for obtaining consistent and reliable results in subsequent tests [38]. Although OCP does not provide quantitative data on the kinetics of corrosion processes, it serves as a predominantly qualitative technique that offers insight into the initial electrochemical behavior of the material [30]. As such, it is commonly applied as the first step in standardized corrosion testing protocols [30].

Figure 2 presents the OCP values of S235JR steel immersed in 0.5 M HCl solution, measured before and after corrosive tests conducted over exposure periods of 2, 4, 8, 12, and 24 weeks in a corrosive environment. Upon initial immersion in the acidic electrolyte, the OCP exhibits a decrease, followed by stabilization over time. The original OCP data values corresponding to Figure 2 are provided in Figure S1.

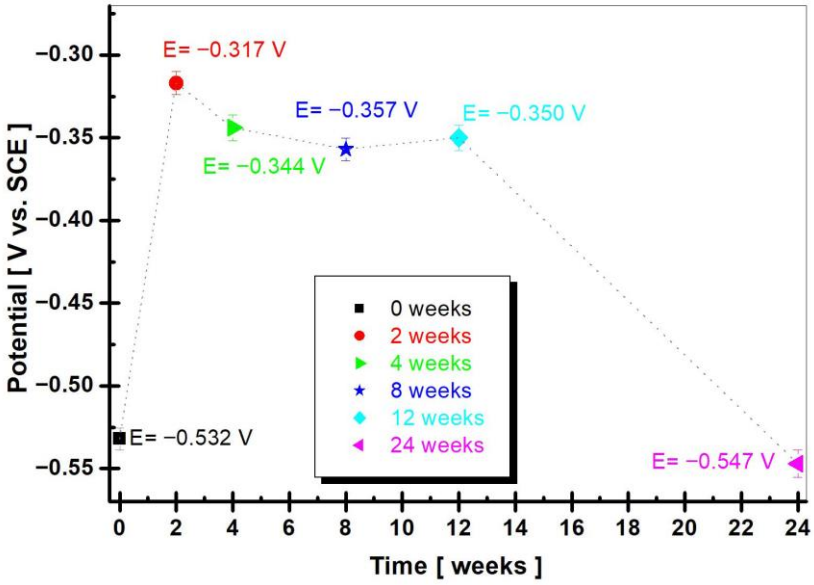


Figure 2. Open circuit potential of S235JR steel samples during 24 weeks of exposure in 0.5 M HCl.

This trend can be attributed to the initial chemical attack by aggressive chloride ions and the surface activation due to metal dissolution [30]. The subsequent stabilization of the potential is likely associated with the formation of corrosion products on the steel surface, which may partially hinder further metal degradation.

The open circuit potential (OCP) values exhibited a gradual shift toward more positive potentials during the initial minutes of immersion, reaching a quasi-stable state after approximately 30 min. After one hour of exposure to the 0.5 M HCl solution, the OCP values of all tested S235JR steel samples were observed to stabilize, indicating the attainment of a steady-state electrochemical condition.

The most negative OCP value, measured at -0.547 ± 0.006 V, was recorded for the sample exposed for 24 weeks, suggesting that prolonged immersion in the corrosive environment increases the thermodynamic susceptibility of the steel to corrosion. The general trend of the OCP indicates a potential increase after 8, 12, and 4 weeks of immersion, with the highest (least negative) OCP value of -0.317 ± 0.009 V registered for the sample immersed for 2 weeks in 0.5 M HCl.

This evolution of OCP can be attributed to the formation and degradation of corrosion product layers. In the early stages (up to 2 weeks), the presence of a relatively compact and adherent layer of corrosion products likely provides a temporary protective barrier, reflected in the less negative OCP values. However, with extended exposure, this layer becomes unstable or is partially removed, exposing fresh metal surface to the electrolyte and resulting in more negative OCP values, as observed after 24 weeks. A similar trend, including fluctuations in the open-circuit potential (OCP), has also been reported in the literature by other authors studying the time-dependent corrosion behavior of carbon steel in 3.5% NaCl solutions and drinking water [9].

3.2.2. Polarization Resistance (R_p) and Corrosion Rate (V_{corr})

General corrosion rate assessments often rely on external polarization techniques, whereby the measured current response is used to calculate the polarization resistance (R_p) in real time and directly. The R_p method represents a widely used electrochemical technique for corrosion monitoring, as it enables the evaluation of the instantaneous corrosion rate at the metal electrolyte interface. Specifically, the polarization resistance reflects the systems resistance to charge transfer during corrosion processes and is inversely proportional to the corrosion current density, which characterizes the electrochemical activity of the metal surface in contact with the corrosive medium [39]. The corrosion rate expressed in micrometers per unit time represents a fundamental quantitative parameter for evaluating the degradation of metallic materials in corrosive environments [39]. The temporal assessment of corrosion rate enables a systematic evaluation of the materials durability under prolonged chemical stress and serves as a predictive tool for estimating its service lifetime in acidic environments [39]. The observed variations in corrosion rate throughout the exposure period may also offer insights into the evolving stability of the material and its capacity to withstand extended operation without critical loss of integrity [9,30,39,40].

Figure 3 illustrates the evolution of polarization resistance values (R_p) and corrosion rate (V_{corr}) for S235JR steel samples exposed to a 0.5 M HCl solution over a period of 24 weeks. The original Rp data values corresponding to Figure 3a are provided in Figure S2. As immersion time increases, changes in R_p values provide insight into the progression of the corrosion process and the development or degradation of protective surface layers. The ability of the R_p technique to provide direct, real-time information makes it particularly suitable for long term corrosion monitoring applications in aggressive environments.

The data presented in Figure 3a indicate a fluctuating trend in the polarization resistance (R_p) values of S235JR steel samples during 24 weeks of immersion in 0.5 M hydrochloric acid (HCl). The initial polarization resistance measured at the beginning of immersion was $77.53 \pm 1.08\ \Omega{\cdot}cm^2$. After 2 weeks, R_p decreased sharply to $15.16 \pm 0.41\ \Omega{\cdot}cm^2$, followed by a significant increase to $60.67 \pm 1.69\ \Omega{\cdot}cm^2$ at 4 weeks. Subsequently, R_p values

progressively declined 26.57 ± 0.54 Ω·cm^2 at 8 weeks, 20.33 ± 0.86 Ω·cm^2 at 12 weeks, and finally 9.93 ± 0.18 Ω·cm^2 after 24 weeks of exposure.

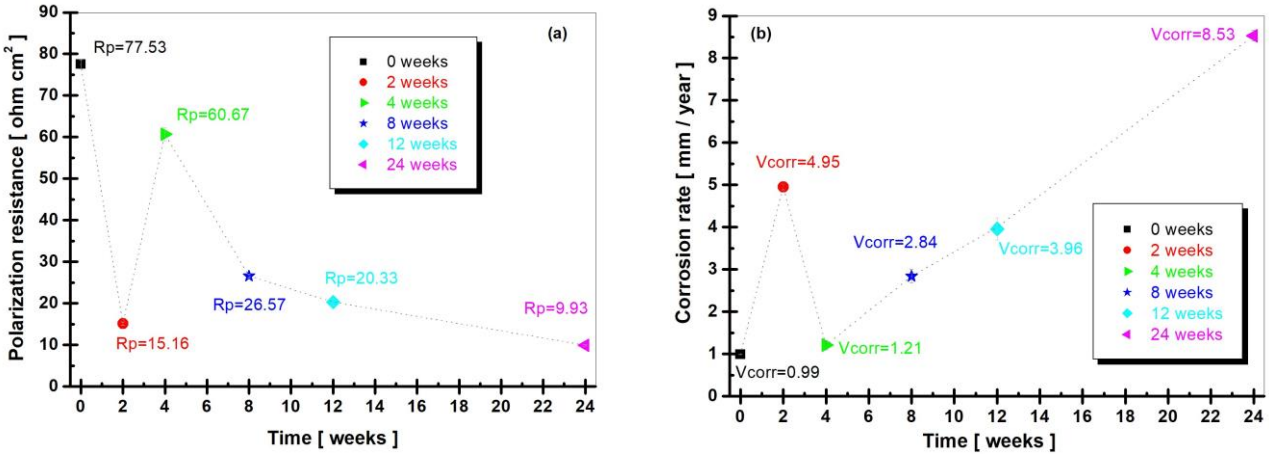


Figure 3. Evolution of S235JR steel samples during 24 weeks of exposure in 0.5 M HCl: (**a**) polarization resistance and (**b**) corrosion rate as penetration rate.

This fluctuating behavior of the R_p values indicates that the corrosion process in 0.5 M HCl is governed by dynamic surface reactions, rather than a steady increase or decrease in corrosion resistance over time. In the early stages of immersion, corrosion products may form a temporary passive layer, provide partial protection and lead to increased R_p values. However, in an aggressive acidic environment such as 0.5 M HCl, this layer is unstable and subject to degradation or detachment over time, resulting in decreased polarization resistance [39–41].

Similar behavior has been reported in literature by Noor and Al-Moubaraki et al. [41] which investigated the corrosion behavior and mechanism of mild steel in HCl solutions with concentrations ranging from 0.25 to 2.5 mol dm^{-3}. Their work demonstrated that mild steel exhibits significant fluctuations in electrochemical parameters due to the transient formation of weakly adherent corrosion product films. These films, being mechanically unstable and prone to dissolution in aggressive chloride environments, provide only limited protection, resulting in oscillations in corrosion resistance and corrosion rate over time [41].

Therefore, the observed fluctuations in R_p over the 24 weeks immersion period are characteristic of an unstable corrosion system, influenced by the alternating processes of localized passivation and reactivation that are typical of carbon steel in acidic environments [39,41].

The corrosion rate of S235JR steel samples immersed in a 0.5 M HCl solution exhibited notable fluctuations over the 24-week exposure period (Figure 3b). The original Vcorr data values corresponding to Figure 3b are provided in Figure S3. Initially, the corrosion rate was 0.99 ± 0.004 mm/year, increasing sharply to 4.95 ± 0.27 mm/year after 2 weeks. A subsequent decrease was observed in week 4, with the rate dropping to 1.21 ± 0.11 mm/year.

After 8 weeks, the corrosion rate rose again to 2.84 ± 0.16 mm/year, followed by a further increase to 3.96 ± 0.3 mm/year at week 12. The highest corrosion rate was recorded at the end of the immersion period, reaching a maximum value of 8.53 ± 0.13 mm/year after 24 weeks of continuous exposure.

These variations in corrosion rate are primarily attributed to the aggressive nature of chloride ions (Cl^-) in the acidic environment [39]. The presence of chloride anions promotes localized breakdown of the protective corrosion product layer, facilitating the initiation and

propagation of corrosion. As the protective layer becomes increasingly compromised, the exposed metallic surface area expands, accelerating the corrosion process [39].

Moreover, the gradual depletion or destabilization of corrosion products contributes to sustained metal dissolution, which in turn leads to a progressive increase in corrosion rate over time [40,41].

3.3. Surface Characterization and Elemental Analysis

The surface morphology and elemental analysis of S235JR steel samples was examined using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) before and after exposure to 0.5 M HCl solution for 2, 4, 8, 12, and 24 weeks.

The corresponding SEM images are presented in Figure 4, while the EDS analysis results are summarized in Table 4. EDS measurements were conducted on the SEM micrographs acquired at a magnification of 500×, allowing representative elemental characterization of the observed surface morphological features.

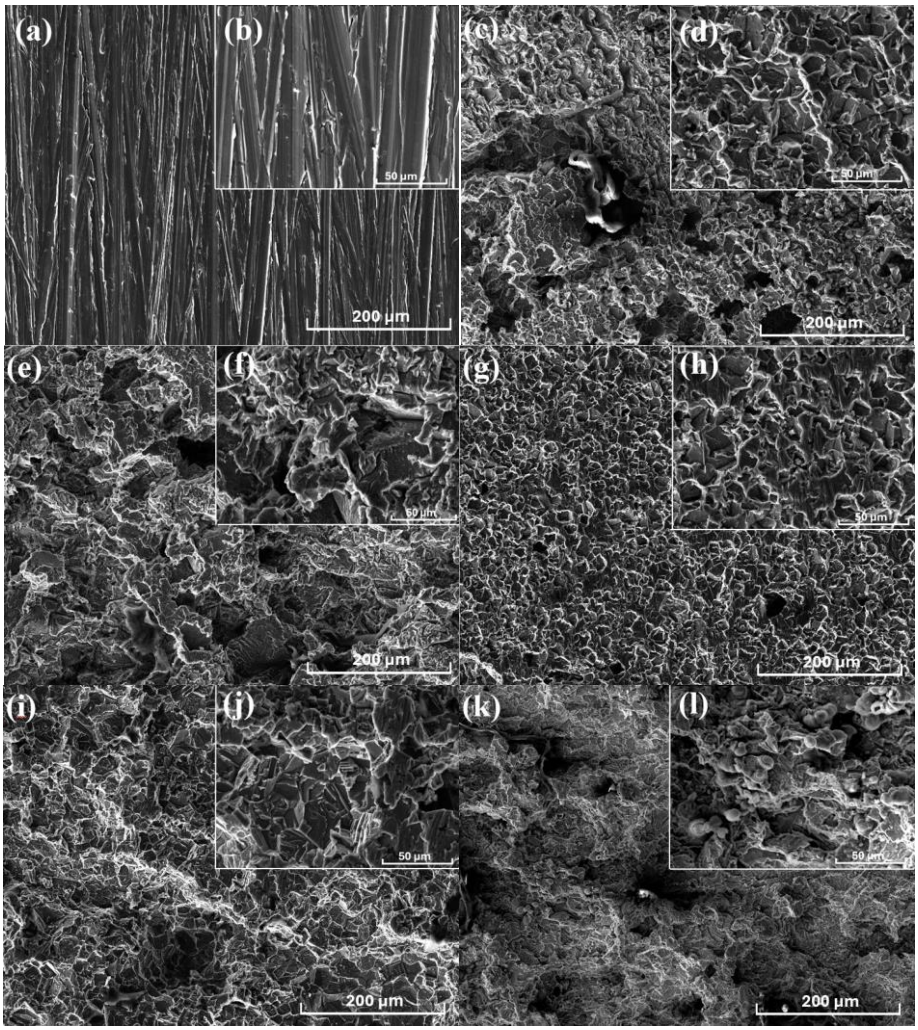


Figure 4. SEM images of the S235JR steel samples before corrosion (**a**), after 2 weeks (**c**), 4 weeks (**e**), 8 weeks (**g**), 12 weeks (**i**) and 24 weeks (**k**) of immersion in 0.5 HCl at 500× and (**b**,**d**,**f**,**h**,**j**,**l**) at 2000×.

SEM analysis revealed that the surface of the S235JR steel prior to corrosion testing was relatively smooth and free of visible defects. However, after exposure to the 0.5 M HCl solution, the formation of cracks and deep pits was observed, indicating localized attack induced by the aggressive chloride containing environment.

Table 4. EDS analysis of S235JR steel surface composition before and after exposure to 0.5 M HCl at different immersion periods.

Chemical Elements	Period of Immersion [Weeks]					
	0 (Before Corrosion)	2 (After 2 Weeks)	4 (After 4 Weeks)	8 (After 8 Weeks)	12 (After 12 Weeks)	24 (After 24 Weeks)
Fe (wt%)	99.4	77.1	86.3	83.3	79.1	70.7
O (wt%)	0.6	21.6	13.0	15.1	19.7	26.6
Cl (wt%)	0.0	1.4	0.7	1.7	1.1	2.8

The EDS spectra of the raw data presented in the Table 4 are presented in Figure S4. EDS analysis confirmed a marked increase in chlorine content on the surface of S235JR, indicating the accumulation of chloride ions. At the same time, an increase in oxygen was observed.

This behavior can be described as a balance between strong acidic attack driven by proton reduction and hydrogen evolution and the formation of a porous salt surface film.

This film provides only temporary and incomplete protection, explaining why pits and cracks progressively evolve during testing. Over time, the dynamic competition between salt film formation and its chloride induced breakdown leads to sustained localized degradation of the steel surface, confirming that while the salt film mitigates corrosion to some degree, it cannot provide long term protection in such an aggressive environment [39–42].

3.4. Roughness and Vickers Hardness

A major consequence of alloy corrosion is the progressive degradation of mechanical properties, which can lead to unexpected failures during service. In steel, corrosion not only reduces the effective cross-sectional area but can also cause localized defects such as pits or cavities, significantly compromising mechanical performance [8,9,30,39]. Therefore, investigating the influence of corrosion on the mechanical behavior of S235JR structural steel, particularly in acidic environments, is crucial for assessing long term reliability.

In this study, the effect of corrosion was evaluated by exposing S235JR steel samples in 0.5 M HCl solution for various time intervals: 2, 4, 8, 12, and 24 weeks. Surface degradation was assessed by measuring surface roughness parameters (Ra, Rz, Rq, Rt), with the results summarized in Table 5. These parameters reflect the evolution of surface topography due to corrosive attack and its potential impact on material performance.

Table 5. Roughness measurements values of S235JR steel, before and after corrosion in 0.5 M HCl.

Period of Immersion	Roughness Parameters [μm]			
	Ra	Rz	Rq	Rt
0 (initial)	0.91 ± 0.05	8.75 ± 0.61	1.11 ± 0.08	9.71 ± 0.23
2 (after 2 weeks)	2.92 ± 0.21	21.24 ± 1.02	3.87 ± 0.21	30.42 ± 2.45
4 (after 4 weeks)	8.05 ± 0.57	49.10 ± 3.21	10.64 ± 0.83	58.40 ± 3.12
8 (after 8 weeks)	3.76 ± 0.24	25.47 ± 1.13	4.97 ± 0.31	53.16 ± 3.05
12 (after 12 weeks)	7.57 ± 0.58	48.71 ± 3.17	10.08 ± 0.82	61.73 ± 4.78
24 (after 24 weeks)	9.03 ± 0.65	44.09 ± 2.88	10.79 ± 1.16	66.24 ± 5.02

Additionally, to assess the effect of corrosion on local mechanical behavior, microhardness (Vickers) measurements were performed, and the values are presented in Table 6.

Table 6. Vickers hardness measurements values of S235JR steel, before and after corrosion in 0.5 M HCl.

Period of Immersion	Vickers Hardness, HV0.5
0 (initial)	148.7 ± 3.2
2 (after 2 weeks)	94.6 ± 2.6
4 (after 4 weeks)	96.0 ± 2.8
8 (after 8 weeks)	95.5 ± 2.8
12 (after 12 weeks)	83.8 ± 1.9
24 (after 24 weeks)	87.3 ± 2.1

The combined analysis of surface roughness and microhardness provides a comprehensive understanding of how corrosion alters both the surface structure and the mechanical integrity of S235JR steel, offering valuable understanding for predicting material behavior in aggressive environments.

As shown in Table 5, the surface of the S235JR steel before immersion is smooth, with visible polishing traces and an average roughness (Ra) of 0.91 ± 0.05 µm. After exposure in 0.5 M HCl solution, the surface morphology becomes significantly rougher, characterized by irregular cavities. The average roughness reaches a maximum value of 9.03 ± 0.65 µm after 24 weeks of immersion, indicating substantial surface degradation due to corrosion.

The Ra values do not exhibit a consistent increasing or decreasing trend over time. For instance, after 2 weeks of immersion, Ra increases to 2.92 ± 0.21 µm, and further to 8.05 ± 0.57 µm after 4 weeks, followed by a drop to 3.76 ± 0.24 µm at 8 weeks. Subsequently, the value increased again to 7.57 ± 0.58 µm at 12 weeks and peaked at 9.03 ± 0.65 µm after 24 weeks. This fluctuation suggests that the formation of surface film salts on the steel surface can temporarily inhibit corrosion by forming a protective layer, although the corrosion process continues over time.

The Rt parameter, which represents the maximum height of the roughness profile (peak to valley distance), increases steadily throughout the immersion period from 9.71 ± 0.23 µm initially to 66.24 ± 5.02 µm after 24 weeks. This continuous increase values confirms severe corrosion of the steel surface by the acidic environment.

The increasing surface roughness is directly associated with the progression of corrosion, as rougher surfaces are more susceptible to localized corrosion such as pitting [29,33]. Surface roughness influences the corrosion potential and facilitates the initiation and propagation of corrosion pits [30,34].

As shown in Table 6, the Vickers hardness values of S235JR steel samples tested in 0.5 M HCl solution range from 148.7 ± 3.2 HV0.5 before the corrosion tests to 87.3 ± 2.1 HV0.5 after 24 weeks of immersion. According to the data, a significant reduction in hardness by approximately 50 units is observed after only 2 weeks of exposure to the corrosive environment.

Between 2 and 8 weeks of immersion, the Vickers hardness remains relatively stable, indicating a temporary equilibrium possibly due to the formation of a passive corrosion product layer that partially inhibits further degradation. After 12 weeks, the hardness decreases further, reflecting continued material deterioration. After 24 weeks, a slight increase in hardness is noted, which may be attributed to the accumulation and compaction of corrosion products on the steel surface.

The slight variations in Vickers hardness observed during the exposure period can be attributed to the counterplay between the protective salt film formed on the S235JR steel surface and its localized dissolution, resulting in a non-uniform distribution of corrosion products. These inconsistencies influence the localized mechanical response of the material during microhardness testing.

The decrease in Vickers hardness over time is consistent with the progressive material loss and structural weakening due to acid induced corrosion in the 0.5 M HCl environment.

4. Conclusions

This study provided an in-depth assessment of the long-term corrosion behavior of S235JR carbon steel immersed in 0.5 M HCl solution over a 24-week period by combining gravimetric techniques, electrochemical analysis, surface characterization SEM, and mechanical property assessment through microhardness and roughness measurements.

Gravimetric analysis demonstrated a decreasing trend in corrosion rate, from an initial value of 2.36 mm/year after 2 weeks to 0.47 mm/year at 24 weeks, attributable to the gradual accumulation of corrosion products that act as a partial diffusion barrier to aggressive ionic species. Despite the apparent decline in corrosion rate, localized degradation persisted, indicating incomplete passivation and the dynamic nature of surface reactivity under acidic conditions.

Electrochemical measurements supported the gravimetric results, revealing fluctuating polarization resistance (R_p) and corrosion rate (V_{corr}) values over time. Open circuit potential (OCP) values shifted toward more negative potentials with extended exposure, reflecting increased thermodynamic susceptibility to anodic dissolution. Polarization resistance exhibited variations, indicative of the transient formation and subsequent destabilization of corrosion product layers. The corrosion rate, reaching 8.53 mm/year at 24 weeks, highlights the severity of material degradation in chloride containing acidic environments.

SEM and EDS analysis confirmed the progressive deterioration of the steel surface, intergranular cracks, and surface corrosion products (chlorine, oxides). EDS analysis revealed a significant increase in chlorine and oxygen content, indicating the accumulation on the steel surface of the corrosion products. These morphological transformations align with the topographical changes quantified by surface roughness analysis, where Ra increased from 0.91 μm to 9.03 μm.

Vickers microhardness testing confirmed the negative effect of prolonged exposure to acidic environments on the mechanical integrity of S235JR steel. A significant reduction in hardness, from 148.7 HV0.5 to 87.3 HV0.5, was observed at the end of the immersion period. This reduction is attributed to the loss of metallic substrate and microstructural damage. S235JR carbon steel exhibits considerable susceptibility to corrosion induced degradation in hydrochloric acid environments, manifested by electrochemical instability, morphological deterioration, and mechanical degradation. This study highlights the critical need for protective strategies in acidic conditions.

Future work will focus on the evaluation of green corrosion inhibitors derived from plant extracts and bio-based compounds. These will be investigated for their adsorption behavior, inhibition efficiency, and synergistic effects, with the aim of decreasing steel corrosion while minimizing ecological impact.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/met15101092/s1, Figure S1: Open circuit potential of S235JR steel samples during 24 weeks of exposure in 0.5 M HCl. Figure S2: Polarization resistance of S235JR steel samples during 24 weeks of exposure to 0.5 M HCl. Figure S3: Corrosion rate as penetration rate of S235JR steel samples during 24 weeks of exposure to 0.5 M HCl. Figure S4: EDS spectra–qualitative chemical analysis of the S235JR steel samples before corrosion (a), after 2 weeks (b), 4 weeks (c), 8 weeks (d), 12 weeks (e) and 24 weeks (f) of immersion in 0.5 HCl.

Author Contributions: Conceptualization, A.C.M. and N.B.; methodology, A.C.M., D.L.B., V.G., E.E.H. and N.B.; software, E.E.H.; validation, D.L.B. and V.G.; formal analysis, A.C.M.; investigation, N.B.; resources, A.C.M. and N.B.; data curation, E.E.H.; writing—original draft preparation, A.C.M.

and N.B.; writing—review and editing, A.C.M. and N.B.; visualization, D.L.B.; supervision, A.C.M.; project administration, N.B.; funding acquisition, N.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by "Dunărea de Jos" University of Galati, Romania, grant research no. 7951/31.03.2025.

Data Availability Statement: The original contributions presented in this study are included in the article/supplementary material. Further inquiries can be directed to the corresponding author.

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

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