

Corrosion Behavior of L80 Steel in CO₂ Saturated Brines: Effect of Electrolyte Composition and Temperature in Oilfield Conditions

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How to cite this paper: Chouola, L.S.W., Fothe, H.T., Mouangue, M.R. and Dikwa, J. (2026) Corrosion Behavior of L80 Steel in CO₂ Saturated Brines: Effect of Electrolyte Composition and Temperature in Oilfield Conditions. *Journal of Materials Science and Chemical Engineering*, 14, 81-102. <https://doi.org/10.4236/msce.2026.1410004>

Received: September 11, 2026

Accepted: October 18, 2026

Published: October 21, 2026

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Abstract

The present work explores the corrosion behavior of L80 steel in chloride-based brines (NaCl, KCl, and CaCl₂) under fluctuating temperature and pH conditions, with direct impact on CO₂-containing oilfield environments. The study is built on the KEM-23ST well operated by Perenco Rio del Rey (Cameroon). Electrochemical measurements, gravimetric analysis, and thermodynamic modeling were joined to clarify corrosion mechanism, with highlighting FeCO₃ film formation. The findings reveal that the electrochemical response entails activation-controlled charge transfer near the corrosion potential coupled with cathodic mass-transport limits. Growing temperature quickens corrosion kinetics, whereas the gradual development of FeCO₃ can rise the impact of diffusion through the corrosion-product layer. Corrosion effect is highly dependent on brine composition. KCl shows the minimum corrosion levels in the reported experimental results while CaCl₂ displays the maximum corrosion levels and lower film stability. The thermodynamic results suggest an increased tendency for FeCO₃ precipitation at elevated temperatures. Taken together, the results provide evidence of a transition from mainly activation-controlled behavior to varied activation-diffusion control as transport limitations and corrosion-product films grow.

Keywords

L80 Steel, CO₂ Corrosion, FeCO₃ Layer, Chloride Brines, Surface Corrosion,

1. Introduction

The durability of casings and production equipment in oil and gas fields remains a critical concern for the energy industry. Carbon steels, particularly API 5CT grades such as L80, are widely used in casing applications due to their favorable combination of mechanical strength, cost, and service suitability. However, prolonged exposure to environments containing carbon dioxide (CO₂), hydrogen sulfide (H₂S), and concentrated brine leads to complex corrosion phenomena that can compromise well integrity [1] [2]. CO₂ induced corrosion, often referred to as sweet corrosion, results from the dissolution of CO₂ in aqueous media, followed by the formation of carbonic acid, which serves as a cathodic active species. The anodic dissolution of iron generates ferrous ions (Fe²⁺), which may precipitate as iron carbonate (FeCO₃) under supersaturation conditions. This film can act as a protective layer, limiting electrochemical reactions at the metal/solution interface. Nevertheless, its stability strongly depends on temperature, pH, CO₂ partial pressure, and the ionic composition of the surrounding solution [2]-[5].

Prior studies reported that increasing temperature accelerates electrochemical reaction and mass transport, leading to higher corrosion rates [6]. However, above a critical temperature, typically between 50 °C and 80 °C, the reduced solubility of (FeCO₃) promotes the formation of a more compact and adherent protective layer, which can decrease corrosion rates. The partial pressure of CO₂ (pCO₂) also plays a crucial role by controlling the concentration of dissolved CO₂ and carbonic acid in solutions [7]. An increase in pCO₂ leads to a decrease in pH and an increase in the concentration of electroactive species thereby enhancing corrosion rates [8] [9]. However, at high, pCO₂ the supersaturation of Fe²⁺ and CO₃²⁻ may favor FeCO₃ precipitation, potentially improving surface protection depending on the operation condition. High salt concentrations, brines behave as non-ideal solutions, modifying the activity coefficients of ionic species and influencing chemical equilibria [10] chlorides (Cl⁻), in particular, are known to adsorb on to the steel surface, destabilize protective films, and promote localized corrosion such as pitting. Meanwhile, the nature of the cations (Na⁺, K⁺, Ca²⁺) influences ionic strength and electrochemical kinetics, with divalent ions such as Ca²⁺ generally enhancing corrosion processes due to stronger electrostatic interactions.

In the presence of H₂S sour environments, it promotes the formation of iron sulfide, which can either protect or accelerate corrosion depending on its morphology and adherence. The competition between FeCO₃ and FeS formation is governed by temperature, pH and fluid composition. Even low concentrations of H₂S can significantly affect electrochemical kinetics and increase the risk of localized corrosion and sulfide stress cracking [11] [12]. induce the formation of iron sulfides (FeS), which may alter the morphology and stability of corrosion films.

Thermodynamic competition between FeCO_3 and FeS precipitation depends on operating conditions and fluid chemistry. Even low H_2S concentrations are known to significantly affect electrochemical kinetics, pH, and the risk of localized corrosion or sulfide stress cracking [3] [13]-[19].

To date, a limited number of studies have simultaneously addressed the combined influence of brine composition, temperature, and mixed CO_2 environments on the electrochemical behavior of L80 steel. It is the case of the studies by [20] investigating the effect of salinity on corrosion kinetics found that the corrosion rate decreases as NaCl concentration increases [20], other studies by [21] emphasized the role of temperature and FeCO_3 found that film formation under CO_2 conditions is promoted by higher temperatures and CO_2 partial pressures, resulting in more protective scales [21]. However, these studies were generally conducted under simplified conditions, often focusing on single parameters and predominantly NaCl-based solutions. However, these studies have primarily focused on NaCl solutions, with limited comparative analyses of industrial brines such as CaCl_2 or KCl. In this context, the present study aims to provide a comprehensive experimental and electrochemical investigation of L80 behavior in three representative brines (NaCl, CaCl_2 and KCl) under CO_2 atmospheres [15] [22].

2. Materials and Methods

2.1. Corrosion in Upstream Production System

Corrosion phenomena investigated in this study are representative of conditions encountered in upstream oil and gas production systems. **Figure 1** illustrates a typical oil well configuration, including the wellhead, tubing, production casing, packer, and perforated zones. In such systems, the production tubing commonly manufactured from L80 steel is continuously exposed to aggressive environments containing CO_2 , H_2S and saline formation waters [23] [24]. These fluids flow from the reservoir through the perforations into the production casing and tubing, where pressure and temperature variations promote complex physicochemical interactions. The presence of CO_2 leads to the formation of carbonic acid, while H_2S contributes to sulfide formation, both of which significantly influence corrosion mechanisms. In addition, the composition of formation water, particularly chloride concentration and the nature of dissolved cations (Na^+ , Ca^{2+} , K^+) plays a critical role in determining corrosion severity and scale formation. Therefore, the experimental conditions selected in this work (controlled temperature, $\text{CO}_2/\text{H}_2\text{S}$ environments, and different brine compositions) were designed to simulate realistic downhole conditions, especially those affecting the tubing and production casing materials.

2.2. Material and Sample Preparation

The material investigated in this study is tubing: 3-1/2"9.20 $\neq$ L80 API-NUE carbon steel [25], commonly used in oil and gas well tubing due to its favorable mechanical properties and moderate resistance to corrosion. The chemical composi-

tion of the steel is presented in **Table 1**.

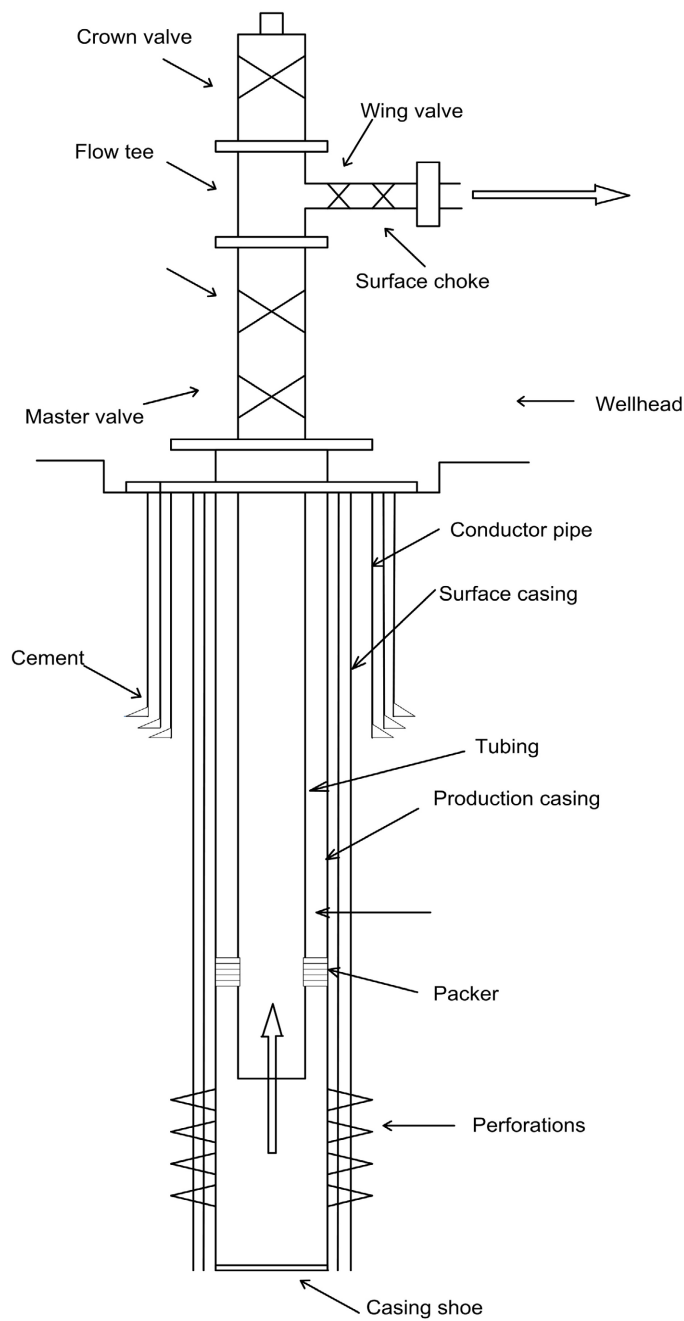


Figure 1. Schematic of a typical oil well.

Table 1. Chemical composition of L80 steel (wt.%).

Element	C	Mn	Si	P	S	Cr	Ni	Mo	Fe
wt. %	0.28	1.40	0.30	0.02	0.015	0.50	0.25	0.15	Balance

Rectangular specimens were machined from L80 Steel and embedded in epoxy resin, leaving an exposed working surface of approximately 1 cm². Prior to each

experiment, the samples were sequentially ground using silicon carbide abrasive papers with grit sizes ranging from 320 to 1200, followed by polishing with alumina suspension to obtain a mirror like surface finish. After polishing, the specimens were thoroughly rinsed with distilled water, degreased with ethanol, and dried in warm air. The prepared samples were immediately immersed in the test solution to minimize surface oxidation prior to measurements. Three brines representative of oilfield formation and completion fluids were prepared using analytical grade salts dissolved in deionized water. The chemical compositions of the tested brine are summarized in **Table 2**.

Table 2. Electrochemical Tafel and Stern-Geary parameters for the tested brines.

Electrolyte	Temperature (°C)	β_a (mV/decade)	β_c (mV/decade)	Stern-Geary Coefficient (mV/decade)
KCl solution	50	130	120	26
	60	98	190	24.9
	80	83	117	22
NaCl solution	50	85	115	18
	60	70	90	14
	80	65	88	16
CaCl ₂ solution	50	49	57	15
	60	46	71	18
	80	45	83	11

All electrolytes were prepared using analytical-grade reagents and deionized water. The brine formulations used in the experimental program were NaCl (0.5 mol/L), KCl brine (specific gravity, sg = 1.02), and a heavy CaCl₂ completion brine (sg = 1.60). Analytical characterization of the KCl brine gave approximately 34,500 ppm Cl⁻ and 19,000 ppm K⁺. The CaCl₂ brine contained approximately 37,000 ppm Cl⁻, 18,500 ppm Br⁻, and 22,000 ppm Ca²⁺. For the 0.5 M NaCl solution, the ideal ionic strength is $I = 0.5$ M. For the field-formulated KCl and CaCl₂ brines, ionic strength was evaluated from the measured ionic composition using $I = 0.5 \sum (c_i z_i^2)$; because only the principal reported ions are available in the analytical summary, the listed ion concentrations are reported explicitly rather than inferring an unverified complete formulation. Initial target pH values ranged from 3.5 to 6.5 and were adjusted using 1 M NaOH. Gas-pressure note: the supplied field documentation reports reservoir pressures of 808 psi (Low Case), 897 psi (Base Case), and 997 psi (High Case) at 1495 mTVDSS. These are field scenario pressures and are not presented as the electrochemical-cell total pressure. A unique H₂S partial pressure was not provided. The main experimental conditions are summarized in **Table 3**.

2.3. Electrochemical Measurements

Electrochemical measurements were performed using a conventional three-elec-

trode cell configuration. The L80 steel specimen served as the working electrode (WE), a saturated Ag/AgCl electrode was used as the reference electrode (RE), and a platinum electrode acted as the counter electrode (CE). Before testing, the brines were actively deaerated for at least 6 h and then brought to the thermostatically controlled test temperature. The field-gas specification used for the corrosion scenario contained CH₄ (85 - 100 mol%), C₂H₆ (0 - 6 mol%), C₃H₈ (0 - 5 mol%), C₄H₁₀ (0 - 3 mol%), C₅H₁₂ (0 - 2 mol%), CO₂ (0 - 2 mol%), N₂ (0 - 3 mol%), and O₂ (0 - 1 mol%), with combined inert compounds limited to 5 mol%. The modeled equilibrium pCO₂ was 0.9 bar at 40°C, 0.8 bar at 60°C, and 0.5 - 0.6 bar at 80°C. H₂S was present as variable trace species associated with reservoir souring, but a unique experimental pH₂S value is not available in the supplied protocol and is therefore not assigned here. For long-term OCP/LPR monitoring, the cell was hermetically sealed after preparation; equilibrium pCO₂ was established from the multiphase simulation used for the test scenario. The electrochemical cell configuration is illustrated in **Figure 2**.

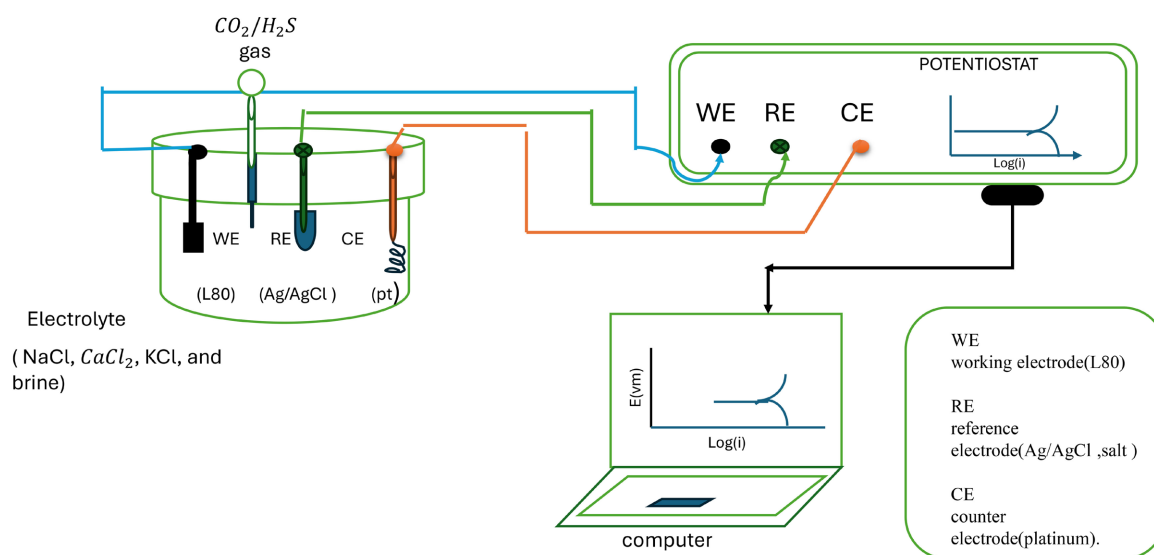


Figure 2. Schematic representation of the electrochemical cell used for corrosion measurements.

The corrosion rate (CR, mm·year⁻¹) was determined using the following relationship:

$$CR = (k \cdot i_{\text{corr}} \cdot EW) / \rho \quad (1)$$

Legend: where $k = 3.27 \times 10^{-3}$ (mm·g·μA⁻¹·cm⁻¹·year⁻¹), i_{corr} is the corrosion current density (μA·cm⁻²), EW is the equivalent weight of the alloy, and ρ is the density on of iron (7.85 g·cm⁻³). For L80 steel, EW= 27.92 g·equiv⁻¹. In addition, polarization resistance (R_p) was determined from the near OCP region of the polarization curves and used to estimate the corrosion current density through the Stern Geary equation:

$$i_{\text{corr}} = B/R_p \quad \text{and} \quad i_{\text{corr}} = (\beta_a \cdot \beta_b) / (2.303 \cdot R_p \cdot (\beta_a + \beta_b)) \quad (2)$$

Legend: where β_a and β_b are the anodic and cathodic Tafel constants, respectively, and B is the Stern Geary constant [26]. After each experiment, the specimens were cleaned using ethanol, rinsed with distilled water, and dried in a desiccator prior to further analysis.

Table 3. Experimental conditions.

Parameter	Value/Range
Temperature	50°C, 60°C and 80°C
Brine conductivity (KCl, NaCl, CaCl ₂)	Conductivity values are reported for each experimental condition; the field brines were KCl (sg 1.02), NaCl (0.5 M), and CaCl ₂ (sg 1.60).
Chlorides	KCl brine: ~34,500 ppm Cl ⁻ ; CaCl ₂ brine: ~37,000 ppm Cl ⁻ ; NaCl: 0.5 M formulation (chloride concentration follows the prepared 1:1 NaCl molarity).
Total dissolved solids (TDS)	Condition-dependent measured values, reported together with conductivity and ionic composition in the experimental dataset.
pH	Initial target range 3.5 - 6.5; adjusted with 1 M NaOH. pH was monitored continuously and allowed to drift without artificial buffering.
Working electrode	API 5CT L80 steel
Reference electrode	Ag/AgCl
Counter electrode	Platinum
Scan rate	0.5 mV/s
Potential range	±250 mV vs. OCP
Exposure time	30 min OCP stabilization; exposure/measurement durations for gravimetric and time-dependent results are specified separately.

2.4. Mechanistic Schematic

The corrosion mechanism of L80 steel in CO₂/H₂S containing brine is illustrated schematically **Figure 3**. The process involves coupled anodic and cathodic reactions occurring at the metal surface [27]-[29].

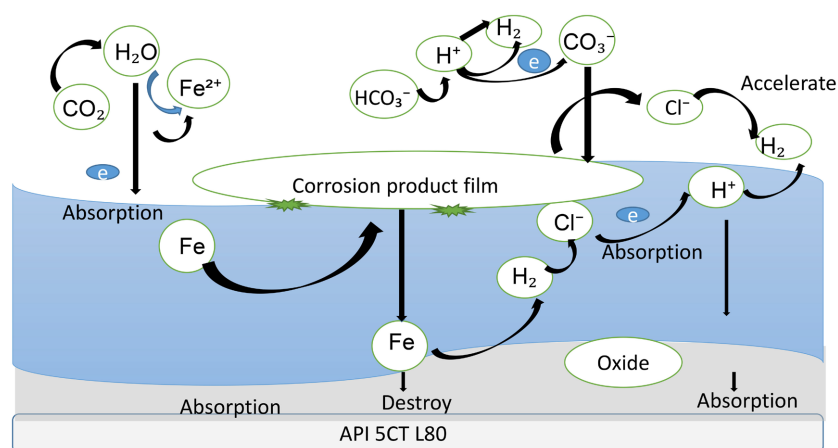


Figure 3. Schematic of L80 corrosion in CO₂/H₂S brines.

The chemical reaction equations from the diagram: The anodic reaction corresponds to iron dissolution: Corrosion begins with the oxidation of metallic iron and is fundamental to the corrosion of L80 steel.



The cathodic reactions include hydrogen evolution and carbonic acid reduction: This reaction is dominant in the presence of dissolved CO_2 and H_2S which acidify the environment. These reactions increase the concentration of H^+ and accelerate corrosion. Proton reduction (acidic environment $\text{CO}_2/\text{H}_2\text{S}$ which)



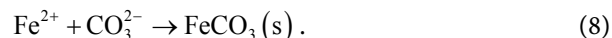
Additionally, dissolved CO_2 reacts with water to form carbonic acid, according to following equilibrium reactions (mild corrosion) [29] [30]:



Carbonic acid (H_2CO_3) subsequently dissociates into hydrogen and bicarbonate ions and then (H^+ and HCO_3^{-}) into hydrogen and carbonate ions (CO_3^{2-})



When the solution becomes supersaturated, ferrous ions (Fe^{2+}) react with carbonate ions (CO_3^{2-}) to form iron carbonate (FeCO_3) also known as siderite:



This compound can form a partially protective layer on the surface of L80 steel under favorable conditions.

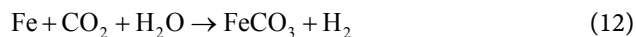
In the presence of hydrogen sulfide (H_2S) iron sulfide may also form. The dissociation of H_2S occurs as follows:



Subsequently, ferrous ion sulfide (FeS):



These corrosion products (FeCO_3 and FeS) can either protect the steel surface or promote localized corrosion depending on their morphology and stability. FeS is generally less protective than FeCO_3 and promotes localized corrosion and hydrogen embrittlement. Overall reaction of corrosion in a CO_2 environment [31]



Overall reaction in H_2S environment



2.5. Thermodynamic Analysis

A thermodynamic analysis was performed to evaluate the stability and formation conditions of corrosion products in the investigated environments. FeCO_3 precip-

itation was assessed using a saturation index based on ionic activities. Temperature, pH, and ionic strength were considered because concentrated brines exhibit non-ideal behavior. Pourbaix diagrams for Fe-CO₂-H₂O and Fe-S-H₂O systems [32] [33] were used to discuss the thermodynamic stability domains of iron species and corrosion products. For a reproducible non-ideal treatment, the activity-coefficient model and its parameters must be stated explicitly, together with the temperature dependence of the FeCO₃ solubility product

$$K_{sp}(T) \cdot SI = \log_{10} \left[\left(a_{\text{Fe}^{2+}} \cdot a_{\text{CO}_3^{2-}} \right) / K_{sp}(T) \right] \quad (14)$$

where $a_{\text{Fe}^{2+}}$ and $a_{\text{CO}_3^{2-}}$ denote the activities of Fe²⁺ and CO₃²⁻, respectively, and $K_{sp}(T)$ is the temperature-dependent solubility product of FeCO₃. The thermodynamic calculations followed the Sun-Nešić formulation, in which the ionic-strength correction is incorporated into the apparent FeCO₃ solubility relation. The correlation used in the MATLAB calculations was: $\log K_{sp}(\text{FeCO}_3) = -59.3498 - 0.041377 T - (2.1963/T) + 24.5724 \log T + 2.518 I^{0.5} - 0.657 I$, where T is the absolute temperature (K) and I is the global ionic strength (mol/L). $SI > 0$ indicates thermodynamic supersaturation with respect to FeCO₃.

3. Results and Discussion

3.1. Physicochemical Evolution of the Brines

The density of various brine solutions was investigated under different conditions, including the presence of calcium chloride (CaCl₂), potassium chloride (KCl), and sodium chloride (NaCl), in an environment where the temperature reached 80°C after 72 hours. The results are presented in **Figure 4**, which illustrates the relationship between density and salt concentration for each brine solution. **Figure 4** shows that CaCl₂ brine exhibits the highest density compared to other chloride-based brines, followed by KCl brine. This observation is consistent with existing literature and reinforces the widespread use of CaCl₂ and KCl as medium to high-density brines in well completion and workover operations [13] [34]. Furthermore, the data reveals that at 28°C, KCl brine reaches a higher maximum density than NaCl brine. This result indicates that KCl is more effective than NaCl in increasing the density of aqueous fluids. Overall, brine density and pH vary significantly with both temperature and ionic composition.

KCl is the most stable brine in terms of both density and pH, making it the most suitable electrolyte for minimizing corrosion of L80 steel. NaCl exhibits intermediate stability, making it suitable for moderately corrosive environments such as wells. In contrast, CaCl₂ is the least stable brine, showing strong acidification, significant density variation, and a catalytic effect on corrosion (as reflected by corrosion rate (CR) and corrosion current density (i_{corr})). The decrease in pH and density is directly correlated with the increase in corrosion rate observed experimentally. **Figure 4** shows that corrosion of L80 steel in CaCl₂ is governed by acid driven kinetics, whereas corrosion in KCl is minimal, confirming trends widely

reported in the literature.

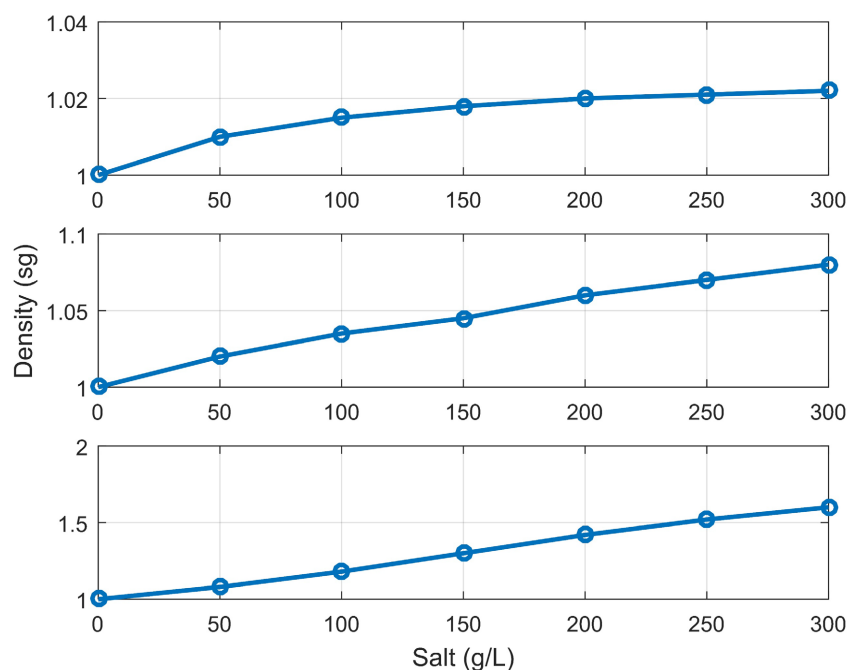


Figure 4. Graph of dissolved salt concentration in water.

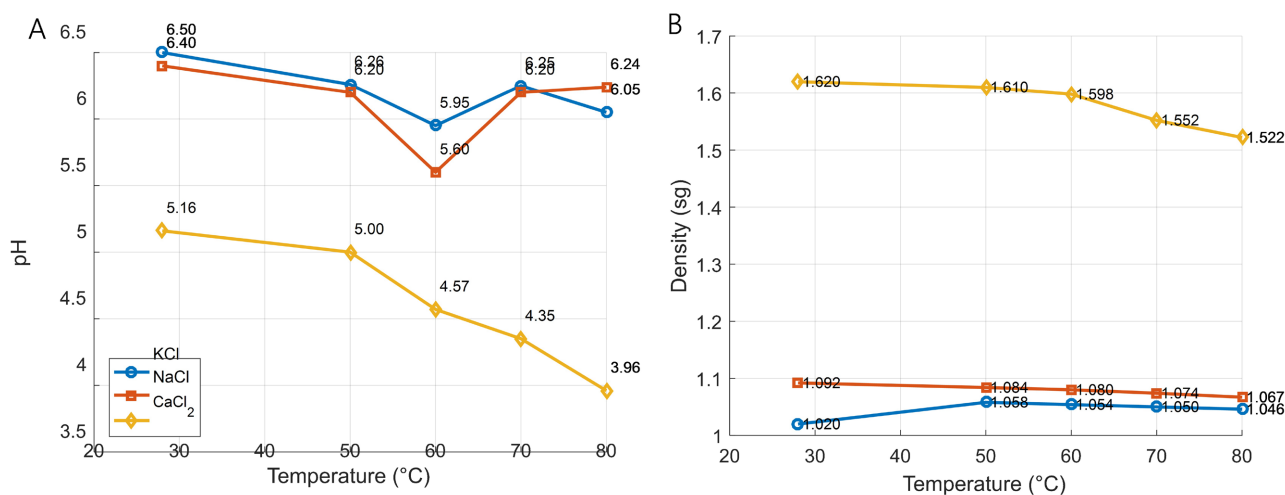


Figure 5. Evolution of density and pH of brines with temperature.

KCl brine exhibits the highest stability in terms of density and pH over the temperature range 50°C - 80°C. Its density remains nearly constant, and its pH shows minimal variation, indicating limited acidification. This behavior reflects lower ionic reactivity and reduced interaction between aggressive species and the metal surface, as shown in **Figure 5**. NaCl brine shows moderate density variations, consistent with its intermediate ionic strength. In contrast, CaCl₂ brine exhibits the largest fluctuations in density and the most significant decrease in pH, indicating strong ion exchange reactions and accelerated acidification. The observed acidifi-

cation in CaCl_2 brine is associated with hydrolysis reactions and the release of acidic species, which reduce solution alkalinity. This effect destabilizes protective corrosion films and enhances steel dissolution. The strong dependence of corrosion on pH is consistent with established mechanisms, where decreasing pH increases carbonic acid concentration and accelerates the cathodic hydrogen evolution reaction.

3.2. Electrochemical Behavior: Polarization Curves

Electrochemical responses were evaluated using potentiodynamic polarization. **Figure 6** shows the polarization curves obtained for L80 steel in NaCl, KCl, and CaCl_2 electrolytes at different temperatures.

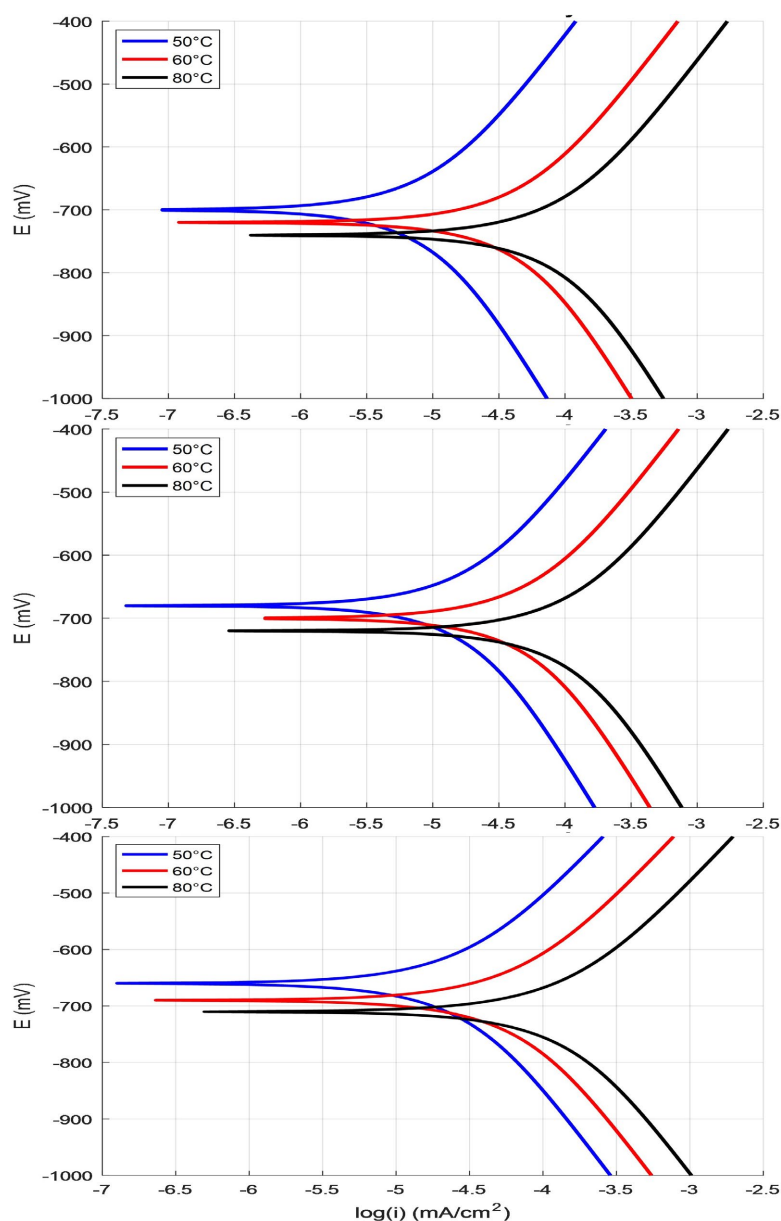


Figure 6. Polarization curves of L80 steel at different temperatures and electrolytes.

Potentiodynamic polarization analysis indicates competition between charge-transfer kinetics, mass transport, and the stability of interfacial corrosion-product films. After the stated OCP stabilization period, E_{corr} values remained within a relatively narrow range across the investigated conditions, while temperature and electrolyte composition modified the polarization response. The interpretation of E_{corr} should therefore be considered together with i_{corr} , Tafel slopes, and the cathodic transport-limited region rather than as an isolated measure of corrosion severity.

The cathodic branch is characterized by a diffusion-limited plateau between -700 and -850 mV, the magnitude of which increases with temperature in accordance with the temperature-dependent laws of diffusion coefficients. Notably, the nature of the cations radically influences anodic dissolution: while KCl promotes the formation of a stable interfacial film, NaCl acts as an intermediate medium, and CaCl_2 ultimately exacerbates iron dissolution. In calcium-rich chloride media, this behavior is punctuated near -500 mV by the emergence of a singular current peak. This phenomenon likely reflects the mechanical rupture of a mixed iron and calcium carbonate layer FeCO_3 and CaCO_3 , preferentially precipitated due to local interfacial alkalization. The instability of this protective film, accentuated by the high ionic strength of the medium, underscores the deleterious role of Ca^{2+} and Cl^- ions in destabilizing passivating phases at high anodic overpotentials.

3.3. Evolution of Corrosion Potential (E_{corr}) and Corrosion Current (i_{corr})

At lower temperature, the Tafel regions indicate an important contribution from activation-controlled charge transfer. The cathodic polarization curves also display a transport-limited region, showing that the process cannot be described as purely activation-controlled over the full potential range. At higher temperature, changes in the anodic and cathodic slopes, together with enhanced transport and corrosion-product development, are consistent with mixed activation-diffusion control. The applicable regime therefore depends on potential, temperature, electrolyte composition, and the extent of surface-film formation.

A shift of E_{corr} toward more positive values is observed with increasing temperature and salinity, indicating an increase in corrosion activity. KCl exhibits the highest E_{corr} values, confirming its lower aggressiveness, while CaCl_2 shows more active corrosion behavior. This trend reflects the modification of electrochemical equilibrium and surface film stability, in agreement with previous electrochemical studies. However, temperature also affects corrosion product stability. The solubility of FeCO_3 decreases with increasing temperature, promoting its precipitation on the steel surface. These results are consistent with previous studies reporting the influence of temperature on FeCO_3 precipitation kinetics [33]. The evolution of the corrosion potential (E_{corr}) of L80 steel in the different electrolytes is presented in **Figure 7**.

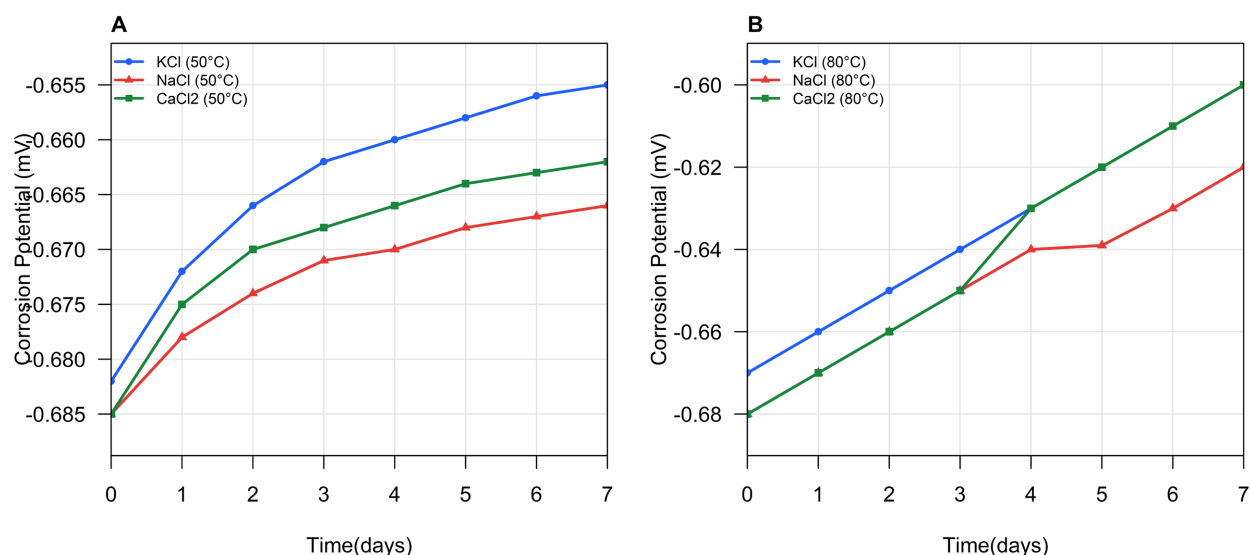


Figure 7. Evolution of corrosion potential (E_{corr}) of L80 steel in different electrolytes.

3.4. Corrosion Rate Analysis and Multifactorial Dependence

The evolution of corrosion rates (CR) is presented in **Figure 8**.

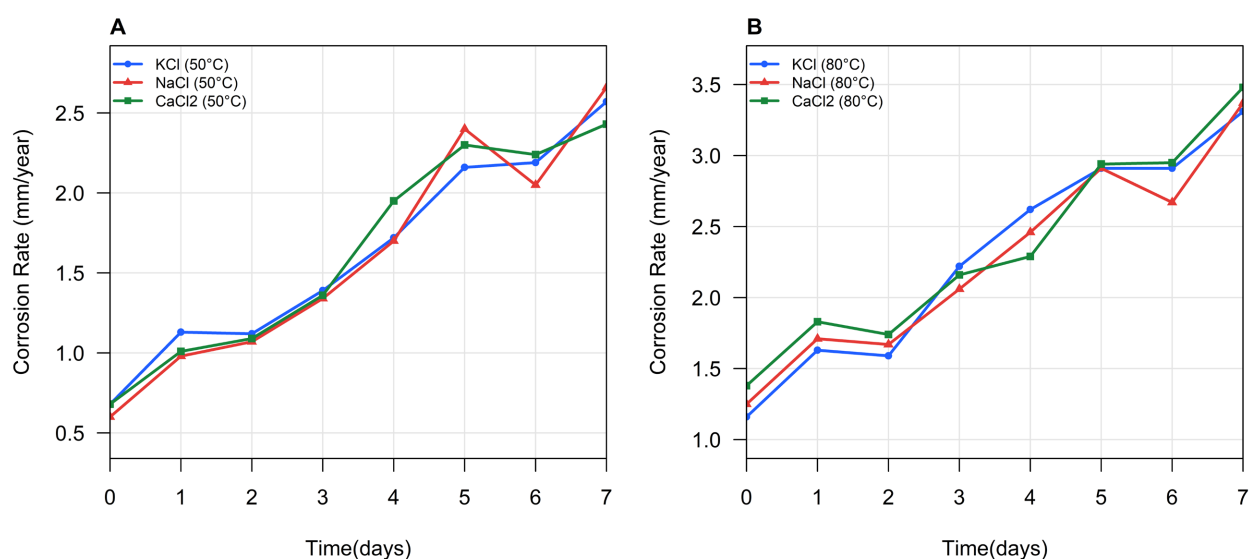


Figure 8. Corrosion rate vs. temperature for L80 steel in different electrolytes.

Corrosion rates (CR, mm/year) and i_{corr} values extracted from polarization curves and LPR measurements are discussed together with the electrochemical results. Across the reported experimental conditions, corrosion rate generally increased with temperature. Electrolyte aggressiveness in the reported experimental dataset followed the order $\text{CaCl}_2 > \text{NaCl} > \text{KCl}$. CaCl_2 produced the highest corrosion rates, whereas KCl showed the lowest values. Time-dependent datasets labelled as prediction are treated as modeled/predicted results and are not used as experimental replicates. An $\text{SI} > 0$ denotes thermodynamic supersaturation.

3.5. Influence of Electrolyte Composition

The effect of brine composition is clearly observed in **Figure 7** and **Figure 8**. NaCl and KCl systems exhibit lower corrosion rates and more stable electrochemical behavior compared to CaCl₂. This difference is attributed to the higher ionic strength of CaCl₂, which increases FeCO₃ solubility and delays its precipitation. The delayed formation of protective films in CaCl₂ brine explains the higher corrosion rates observed. This delayed precipitation can be attributed to increased ionic strength, which enhances FeCO₃ solubility [33].

3.6. Gravimetric Validation (Weight Loss Analysis)

The weight loss measurements presented in **Figure 9** confirm the electrochemical results.

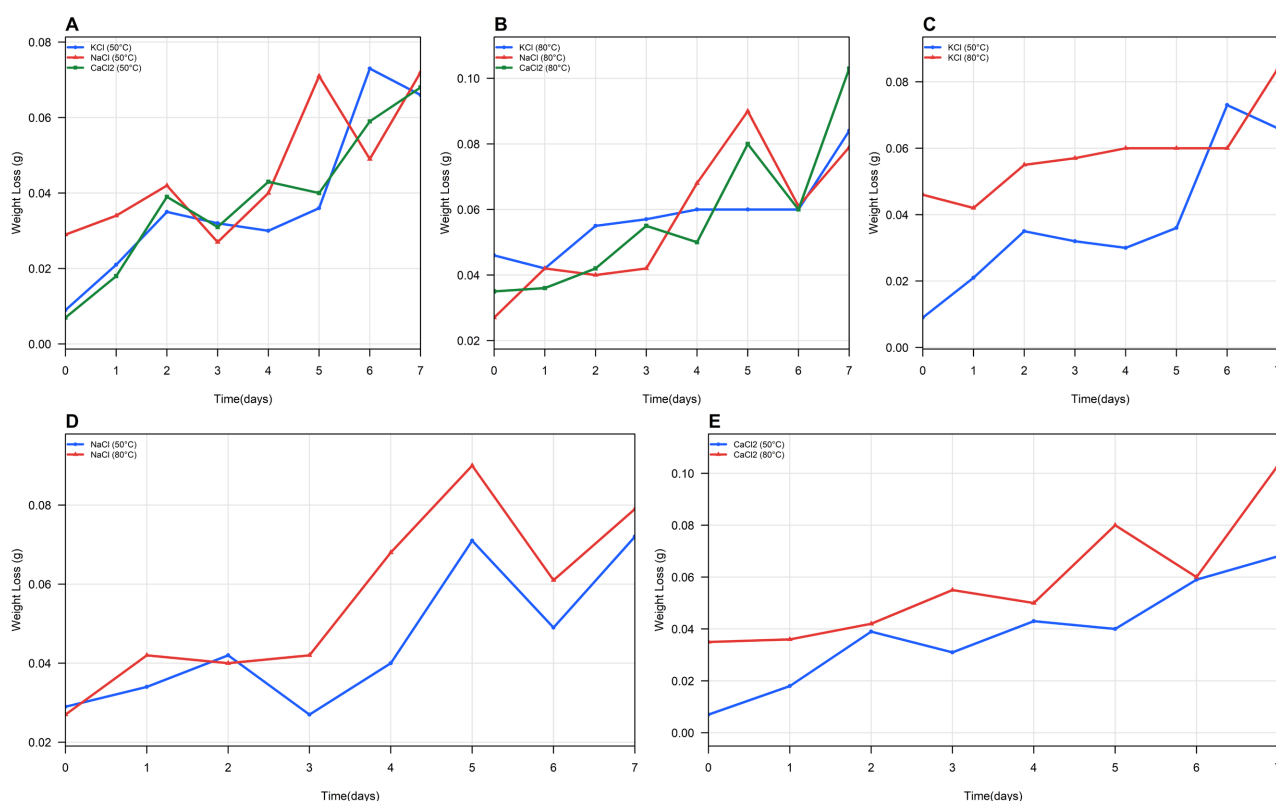


Figure 9. Weight-loss variation of L80 steel as a function of temperature.

Corrosion rate increased significantly from 50°C to 80°C for all electrolytes. At 80 °C the enhancement of mass transport, faster Fe dissolution, and increased molecular diffusion amplified corrosion. However, in KCl and NaCl brines, a partial reduction of the corrosion rate was observed after long exposure (>10 h), indicating the onset of FeCO₃ precipitation and partial surface passivation. The weight loss measurements under different temperatures conditions are grouped in **Figure 9**.

Lower pH caused a strong exponential increase in CR and i_{corr} . At pH = 3.5, all

systems remained in the active corrosion domain, with no evidence of FeCO_3 stabilization. At $\text{pH} = 6.5$, the conditions favored the transition toward the passivation zone predicted by Pourbaix diagrams, especially in KCl and NaCl environments. The effect of pH on the weight-loss response of L80 steel is illustrated in **Figure 10**.

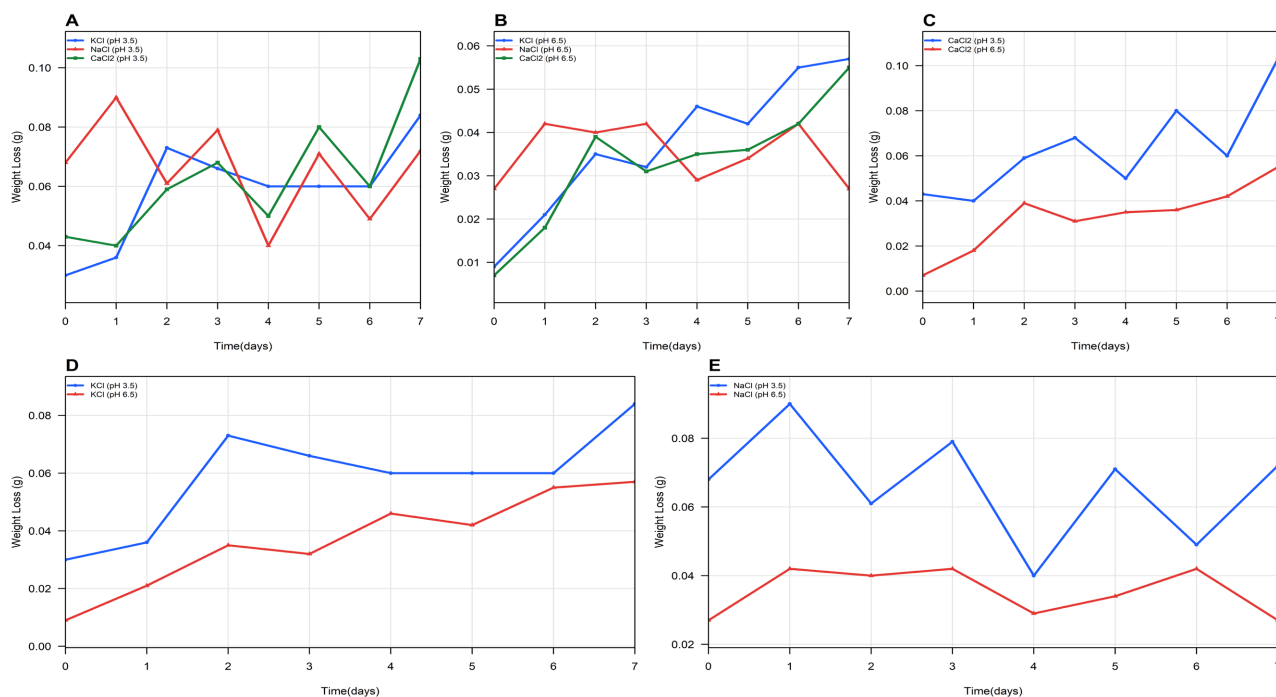


Figure 10. Weight-loss variation of L80 steel as a function of pH.

The results indicate that lower pH values significantly accelerate corrosion, with CaCl_2 producing the highest level of material degradation among the electrolytes investigated. This behavior is attributed to the increased availability of H^+ ions under acidic conditions, which enhances cathodic reactions, particularly the hydrogen evolution reaction, thereby accelerating the overall corrosion process. In addition, the high ionic strength of CaCl_2 further contributes to destabilizing protective films, leading to sustained metal dissolution. These findings are consistent with established corrosion mechanisms in CO_2 containing environments, where carbonic acid plays a central role in promoting steel degradation and controlling electrochemical reactions at the metal solution interface.

3.7. Scale Formation and Salinity Effect

Scale formation increases with salinity, particularly when Fe^{2+} and CO_3^{2-} reach supersaturation. However, scale protectiveness varies significantly. In CaCl_2 and NaCl, the scales are porous, weakly adherent, and easily disrupted by chloride ions, resulting in sustained corrosion. In KCl, the scale is denser and more uniform, providing partial protection.

Higher salinity promotes scale formation, particularly under conditions favor-

able for FeCO_3 precipitation: $\text{Fe}^{2+} + \text{CO}_3^{2-} \rightarrow \text{FeCO}_3(\text{s})$. However, chloride ions reduce the stability of the protective layer, resulting in non-uniform scale formation; Increased localized corrosion; This confirms that scale formation does not necessarily guarantee corrosion protection. Average corrosion rates followed the order: $\text{CaCl}_2 > \text{NaCl} > \text{KCl}$. The variation in corrosion-scale mass with electrolyte type and salinity is shown in **Figure 11**.

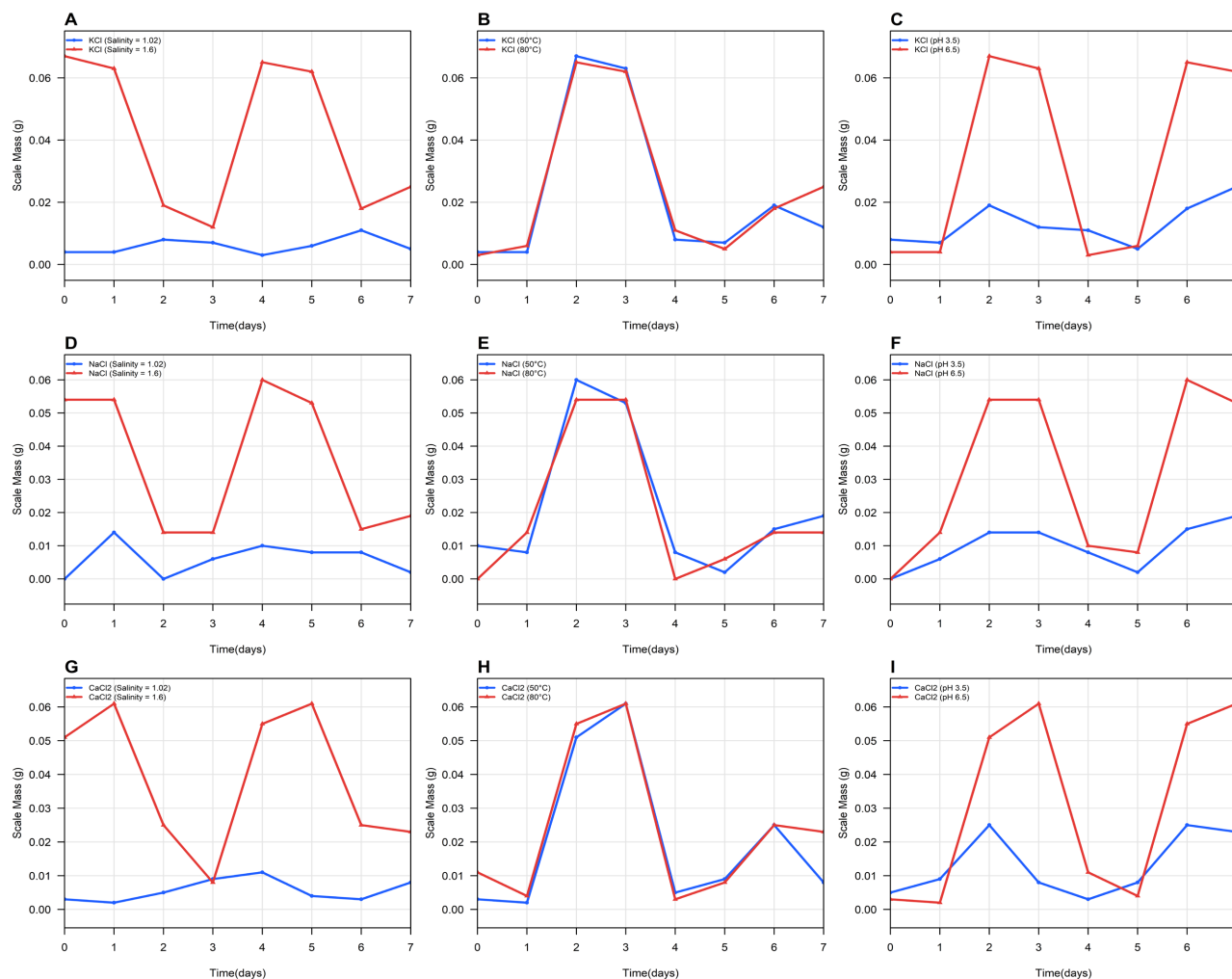


Figure 11. Evolution of corrosion-scale mass with electrolyte type and salinity.

KCl ($\text{CR} \approx 1.8$ mm/year) showed the lowest corrosion, due to stable density, limited acidification, and more coherent film formation. NaCl ($\text{CR} \approx 2.5 - 2.6$ mm/year) presented moderate corrosion, consistent with its typical behavior in CO_2 systems.

CaCl_2 ($\text{CR} > 3.5$ mm/year in the reported high-corrosion conditions) produced the highest corrosion rates. These results were interpreted in relation to Ca^{2+} interactions, ionic strength, and corrosion-product-film stability. Multifactorial analyses were also used to examine the influence of pH, temperature, salinity, and dissolved oxygen. Predicted/model-derived datasets are distinguished from direct

experimental observations and are not treated as experimental replicates.

3.8. Chloride Concentration and Electrolyte Effect

The influence of chloride concentration in different electrolytes is summarized in **Figure 12**.

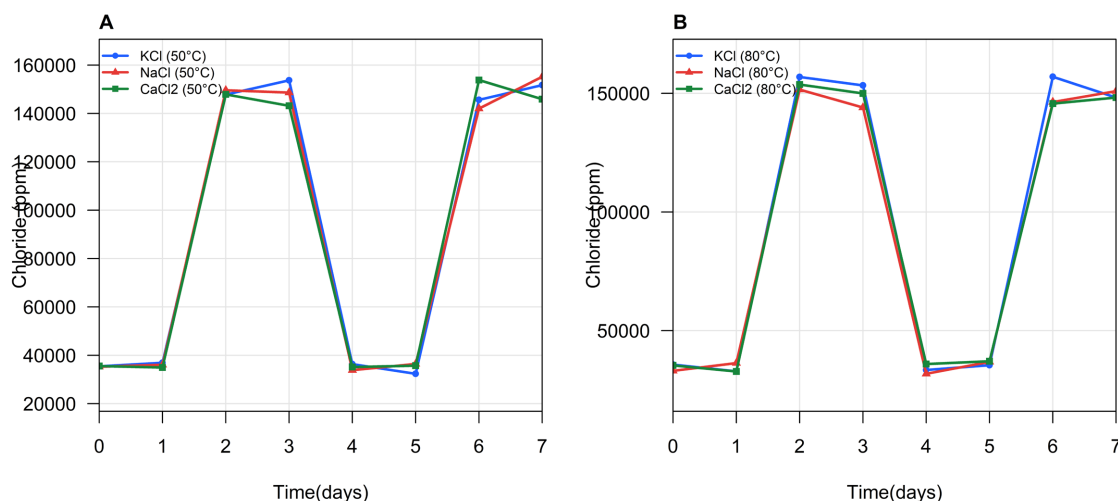


Figure 12. Effect of chloride concentration on corrosion behavior of L80 steel.

Chloride ions can intensify corrosion by increasing electrolyte conductivity and contributing to disruption of surface films. In the reported experimental dataset, CaCl_2 exhibited the greatest corrosion response, NaCl showed intermediate behavior, and KCl showed the lowest corrosion response. Because chloride concentration differs substantially among the tested brines, the observed differences cannot be attributed solely to the cation identity; chloride level, ionic strength, pH, temperature, and film stability must be considered jointly. The thermodynamic evolution of FeCO_3 solubility and saturation is presented subsequently in **Figure 13**.

3.9. Mechanistic Interpretation

The overall corrosion mechanism is summarized in **Figure 3**. At elevated temperature, electrochemical reaction rates and mass transport increase, while FeCO_3 precipitation can become thermodynamically more favorable. The resulting corrosion behavior reflects the balance between activation-controlled charge transfer, cathodic transport limitations, and transport through or breakdown of corrosion-product films. Consequently, the system may evolve from predominantly activation-controlled behavior near OCP toward mixed activation-diffusion control as temperature increases and surface films develop.

3.9.1. Solubility of FeCO_3 (K_{sp}) and Saturation Index (SI)

Figure 13 presents the variation of the solubility product (K_{sp}) of iron carbonate (FeCO_3) as a function of temperature in the range 290 - 360 K for L80 steel. This

evolution highlights two distinct thermodynamic regimes that govern precipitation behavior and corrosion protection. In the temperature range of 290 - 340 K, a pronounced decrease in the solubility product is observed. This trend indicates that the solubility of FeCO_3 decreases significantly as temperature increases, thereby enhancing its thermodynamic stability in the solid state. From a thermodynamic standpoint, the reduction in K_{sp} reflects a decrease in the Gibbs free energy of dissolution, which promotes the precipitation of FeCO_3 . Previous studies S. Nešić and W. Sun have reported similar behavior in CO_2 containing systems, where increasing temperature favors FeCO_3 formation and leads to the development of protective surface layers [6] [9]. Under these conditions, the system rapidly reaches supersaturation, which promotes nucleation and growth of FeCO_3 crystals and contributes to a progressive reduction in corrosion rate. Beyond 340 K, the evolution of K_{sp} becomes relatively stable, with only minor variations observed up to 360 K. This behavior indicates that the system approaches a quasi-equilibrium state in which FeCO_3 becomes only slightly soluble and the influence of temperature on its solubility becomes secondary. In this high-temperature regime, corrosion behavior is no longer controlled primarily by thermodynamics but rather by kinetic processes such as precipitation rate, mass transport, and film restructuring. At these temperatures, FeCO_3 precipitation is rapid and leads to the formation of a dense, adherent, and protective layer on the steel surface. As reported by Nesic [35] [36], above approximately 70°C - 80°C , corrosion control shifts from a thermodynamic regime to a diffusion-limited regime governed by transport through the FeCO_3 film. The overall decrease in the solubility product between 290 and 340 K reflects the increasing stability of FeCO_3 and its strong tendency to precipitate on the L80 steel surface. Above 340 K, the stabilization of K_{sp} indicates that FeCO_3 solubility becomes negligible and that corrosion behavior is primarily governed by the formation, integrity, and protective properties of the corrosion product layer.

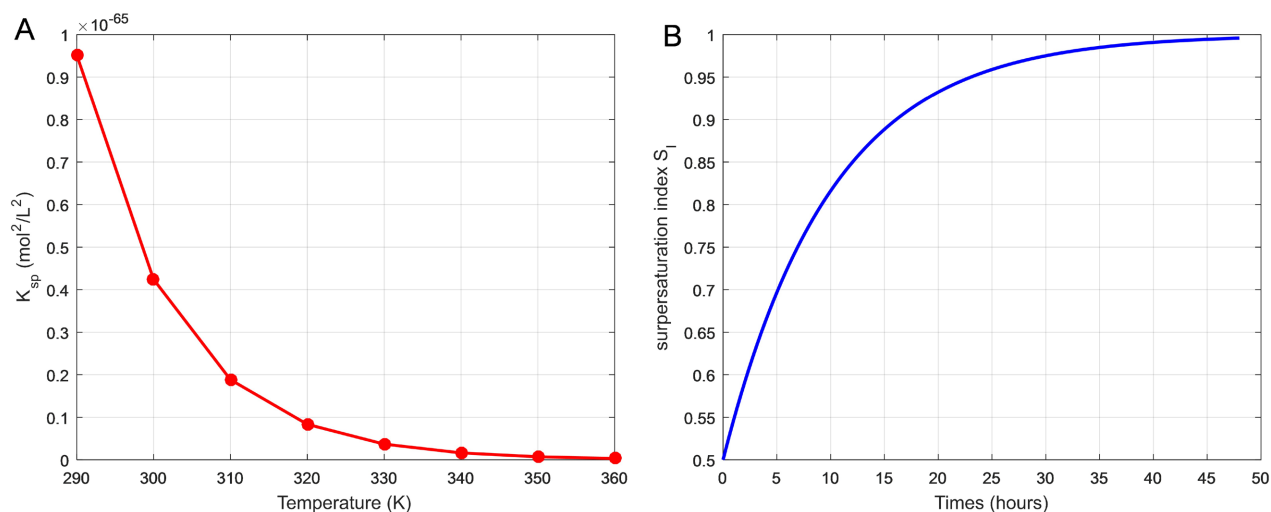


Figure 13. FeCO_3 solubility, Fe^{2+} saturation and SI evolution.

As shown in **Figure 13(A)**, the solubility product (K_{sp}) decreases significantly with increasing temperature, confirming that FeCO_3 becomes less soluble at elevated temperatures. This reduction in solubility promotes precipitation and favors the formation of a protective layer under suitable chemical conditions. Furthermore, **Figure 13(B)** shows that the saturation index (SI) increases progressively with time. When SI exceeds zero, the solution becomes supersaturated and precipitation becomes thermodynamically favorable. At 80°C and pH 6.5, KCl and NaCl systems reach supersaturation earlier and maintain it for a longer duration, allowing the formation of a dense and protective FeCO_3 film. In contrast, the CaCl_2 system exhibits a delayed increase in SI, which is attributed to its higher ionic strength. This elevated ionic strength enhances FeCO_3 solubility and delays the onset of supersaturation, thereby hindering the formation of a stable protective film. As a result, corrosion remains more active in CaCl_2 brines, which is consistent with the experimental observations. The saturation index stabilizes after approximately 24 hours, indicating that the system approaches thermodynamic equilibrium and that the rate of film growth decreases significantly. This stabilization behavior correlates with the lower corrosion rates observed in KCl and NaCl systems and highlights the strong relationship between precipitation kinetics and corrosion protection efficiency.

3.9.2. Practical Implications for Well Integrity

The results highlight important operational implications: KCl is the most suitable brine for completion operations requiring minimal corrosion risk. NaCl is acceptable for wells of moderate corrosion severity. CaCl_2 Brines should be avoided, when possible, due to their strong acidification, destabilization of protective films, and short predicted service life (≈ 3.9 years). Maintaining pH near neutral and minimizing dissolved oxygen are fundamental for extending tubing lifespan. Real time monitoring of Fe^{2+} , pH, and salinity is essential for detecting transitions between active corrosion and passivation domains.

4. Conclusion

This study provides an integrated analysis of the corrosion behavior of L80 steel in chloride-based brines (NaCl, KCl, and CaCl_2) using electrochemical measurements, gravimetric observations, and thermodynamic modeling. The results show that temperature, pH, electrolyte composition, chloride level, ionic strength, and corrosion-product-film stability jointly influence corrosion behavior. Polarization results indicate activation-controlled charge transfer near the corrosion potential together with a cathodic transport-limited region; therefore, the overall mechanism is better described as condition-dependent rather than purely activation-controlled. With increasing temperature and development of FeCO_3 -containing corrosion products, mixed activation-diffusion control can become increasingly important. In the reported experimental results, KCl exhibits the lowest corrosion response, NaCl intermediate behavior, and CaCl_2 the highest corrosion response. Thermodynamic analysis indicates that FeCO_3 precipitation becomes more favor-

able at elevated temperature, but thermodynamic supersaturation alone does not guarantee a compact or protective film. The protective effect also depends on precipitation kinetics, adherence, morphology, and mass transport. These findings emphasize the need to evaluate brine composition together with operating conditions when assessing corrosion risk in L80 steel systems.

Author Contributions

Conceptualization: L.S.W.C., J.D.; Methodology: L.S.W.C., H.T.F.; Investigation: L.S.W.C., M.R.M.; Formal analysis: L.S.W.C.; Writing original draft: L.S.W.C.; Writing review and editing: L.S.W.C., J.D.; Supervision: J.D.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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