

## Corrosion In multiphase flow systems: The impact of high CO<sub>2</sub> and low water conditions

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### Abstract

Corrosion in multiphase flow systems presents a persistent threat to the integrity of oil and gas pipelines, especially under complex operating conditions. This paper investigates internal corrosion mechanisms in environments characterized by high carbon dioxide (CO<sub>2</sub>) levels and low water content—a combination traditionally perceived as less corrosive due to water's essential role in electrochemical degradation. Contrary to conventional assumptions, this study reveals that corrosion can still initiate and propagate under low-water conditions, particularly through the presence of condensed water films and micro-phase separation. The paper provides a detailed analysis of how corrosion manifests in such systems, considering key factors such as flow regime, wall shear stress, and the localized accumulation of aqueous phases. Special attention is given to the formation and stability of iron carbonate (FeCO<sub>3</sub>) scales, which may act as protective barriers or, under specific conditions, degrade into porous, ineffective layers. The interplay of temperature, pressure, and hydrocarbon composition is also examined, highlighting how these variables influence both the likelihood and severity of corrosion in transitional flow regimes. Advanced modeling techniques are employed to improve corrosion rate predictions, accounting for intermittently wetted surfaces and the dynamic behavior of fluids in stratified or slug flow patterns. Laboratory experiments and field data are integrated to validate these models and refine risk assessment tools. The study concludes with recommendations for corrosion monitoring and mitigation in systems where traditional water-dependent models may underestimate risk. These findings contribute to a more nuanced understanding of CO<sub>2</sub> corrosion and support the development of targeted, cost-effective corrosion management strategies in dry or semi-dry pipeline environments.

**Keywords:** Multiphase Flow; CO<sub>2</sub> Corrosion; Water Condensation; Iron Carbonate Scale; Flow Regime; Oil and Gas Pipelines

## 1. Introduction

### 1.1. Background: Corrosion in Oil and Gas Pipelines

Corrosion remains one of the most critical challenges in the oil and gas industry, particularly within pipeline systems transporting multiphase fluids. Internal corrosion, which occurs on the inside wall of a pipeline, compromises structural integrity and operational safety, often resulting in catastrophic failures if not adequately managed. Corrosive environments in hydrocarbon pipelines are typically generated by the presence of acidic gases such as carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S), water content, and impurities, which together drive electrochemical reactions at the pipe-metal interface [1].

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The economic burden of corrosion is substantial, with millions of dollars expended annually on repair, replacement, downtime, and environmental damage mitigation. A single pipeline rupture due to undetected internal corrosion can lead to regulatory fines, reputational harm, and hazardous material spills. Furthermore, corrosion detection and monitoring costs escalate with pipeline length, remote location, and complexity of flow conditions [2].

Conventional mitigation approaches—such as chemical inhibition, material selection, and periodic inspection—are necessary but not always sufficient in dynamically changing flow environments. As pipeline infrastructure ages and exploration moves into more aggressive environments, there is a growing need for deeper understanding and predictive modeling of corrosion mechanisms, particularly under unconventional fluid conditions [3].

Internal corrosion continues to pose a complex threat due to its dependence on numerous factors such as temperature, pressure, fluid chemistry, and flow regime. Accurate prediction models and mechanistic studies remain essential for improving the reliability of corrosion risk assessments, refining inspection intervals, and designing preventive measures that are both technically effective and economically viable [4].

## **1.2. Focus on CO<sub>2</sub> and Low-Water Multiphase Systems**

Traditional corrosion models in oil and gas pipelines often assume that water must be present as a continuous phase for corrosion to initiate and propagate. This assumption forms the basis for many inspection strategies and inhibitor dosing programs. However, emerging studies in low-water multiphase systems reveal that CO<sub>2</sub> corrosion can occur even when the water cut is extremely low, challenging long-standing industry paradigms [5].

In such systems, water may exist as a dispersed phase or be intermittently present due to flow fluctuations. Despite low water saturation, thin water films or microdroplets adhering to the pipe wall may provide sufficient electrolyte for localized corrosion reactions. Moreover, the presence of dissolved CO<sub>2</sub> significantly reduces the pH, promoting the formation of carbonic acid and enhancing corrosion kinetics even in water-lean environments [6].

This phenomenon is particularly concerning in high-pressure, high-temperature (HPHT) gas-condensate pipelines, where CO<sub>2</sub> partial pressures are elevated, and localized condensation may produce corrosive conditions in what appear to be dry segments. The failure to account for these effects can result in underestimation of corrosion risk and premature asset degradation [7].

By re-evaluating the role of CO<sub>2</sub> in low-water systems, this paper aims to advance understanding of internal corrosion behavior under evolving multiphase flow conditions and support more robust mitigation frameworks.

## **1.3. Scope and Article Structure**

This article investigates the role of CO<sub>2</sub>-induced corrosion in oil and gas pipeline systems operating under low water conditions. The objective is to highlight corrosion risks in environments previously considered non-threatening due to the absence of a continuous aqueous phase. The research incorporates a combination of literature review, thermodynamic modeling, and reaction kinetics to explore corrosion behavior across various multiphase scenarios.

The study is structured into multiple sections. Following this introduction, Section 2 provides an overview of corrosion mechanisms specific to CO<sub>2</sub> environments. Section 3 discusses the behavior of water in multiphase flow systems, including droplet formation and wall wetting. Section 4 presents the mathematical modeling of CO<sub>2</sub> corrosion in low-water conditions, incorporating parameters such as pressure, temperature, and water cut. Section 5 validates the proposed model using experimental and field data. Section 6 outlines the practical implications for pipeline design, inspection, and chemical inhibition strategies.

The findings aim to reshape industry assumptions, enhance corrosion prediction accuracy, and inform the development of safer, more cost-effective pipeline integrity programs

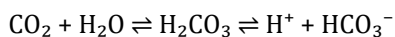
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## **2. Fundamentals of CO<sub>2</sub> corrosion chemistry in multiphase flow**

### **2.1. CO<sub>2</sub> Aqueous Chemistry and Formation of Carbonic Acid**

The onset of carbon dioxide (CO<sub>2</sub>) corrosion in pipeline systems begins with its dissolution in water, forming weak carbonic acid. The chemical equilibrium involved can be expressed as:

CO<sub>2</sub> Aqueous Chemistry and Carbonic Acid Formation:



This reaction sequence highlights the two-step transformation: first, the hydration of dissolved CO<sub>2</sub> to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), and second, the partial dissociation of H<sub>2</sub>CO<sub>3</sub> into hydrogen ions (H<sup>+</sup>) and bicarbonate ions (HCO<sub>3</sub><sup>-</sup>). Although carbonic acid is a weak acid, the presence of H<sup>+</sup> is sufficient to lower pH significantly, which in turn accelerates metal dissolution [5].

The formation of carbonic acid is influenced by temperature, pressure, and pH. At higher pressures, CO<sub>2</sub> solubility increases, driving the equilibrium toward higher carbonic acid concentrations. This is particularly relevant in subsea or deep reservoir pipelines, where elevated CO<sub>2</sub> partial pressures enhance acidification even in low-water environments [6].

At moderate temperatures, carbonic acid dissociates more effectively, sustaining acidic conditions necessary for initiating electrochemical corrosion of carbon steel. Unlike strong acids, carbonic acid exerts a mild but persistent attack, particularly when aided by flow-induced mass transfer that replenishes CO<sub>2</sub> at the wall interface [7].

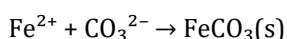
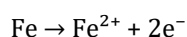
The bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) plays an additional role in buffering pH and interacting with dissolved metal ions to form precipitates. However, it is the concentration of free hydrogen ions that primarily governs the corrosion potential in these systems. Thus, the equilibrium constants of both reactions are critical inputs in predictive corrosion modeling, especially for pipelines where water content is intermittent or limited.

Overall, this aqueous chemistry forms the foundation for CO<sub>2</sub>-induced corrosion mechanisms, linking fluid chemistry to pH shifts and setting the stage for subsequent electrochemical reactions on steel surfaces [8].

## 2.2. Iron Dissolution and Scale Formation

Once the aqueous phase becomes sufficiently acidic due to CO<sub>2</sub> hydration and dissociation, corrosion initiates via electrochemical oxidation of iron at the metal interface. The anodic reaction is given by:

Iron Dissolution and Scale Formation:



Ferrous ions (Fe<sup>2+</sup>) released during this anodic process enter the electrolyte, where they may either diffuse away or participate in further chemical interactions. If carbonate ions (CO<sub>3</sub><sup>2-</sup>) are present—either directly from bicarbonate dissociation or through temperature-driven equilibrium shifts—the following precipitation reaction can occur

Iron carbonate (FeCO<sub>3</sub>), also known as siderite, forms a semi-protective scale on the steel surface. This precipitation is thermodynamically favored under high-temperature, high-pH, and high-Fe<sup>2+</sup> concentration conditions, which are typical in many pipeline systems carrying CO<sub>2</sub>-rich fluids [9].

While FeCO<sub>3</sub> can reduce corrosion by blocking active sites, the quality and adherence of this scale are highly dependent on local flow conditions, surface roughness, and water chemistry. In turbulent or erosive zones, the scale may be disrupted, re-exposing bare metal and allowing corrosion to restart. Conversely, in quiescent sections, scale accumulation can become excessive, leading to flow restriction or solid deposition issues [10].

Importantly, the kinetics of both the anodic iron dissolution and FeCO<sub>3</sub> precipitation are influenced by temperature. As temperature increases, the rate of iron oxidation rises, but so does the tendency for carbonate to precipitate, creating a feedback loop that is not always intuitive. For example, a high corrosion rate may coexist with protective scale under certain operating windows [11].

Understanding the balance between dissolution and precipitation is crucial for designing mitigation strategies, including optimal inhibitor selection, pH adjustment, and flow control. The interaction of iron species with carbonate ions serves as both a corrosion driver and potential inhibitor, depending on environmental parameters.

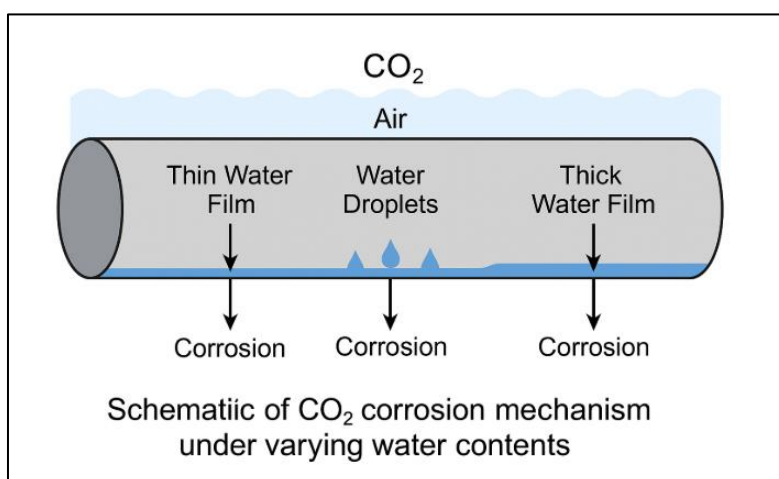
### 2.3. The Role of Water in Electrochemical Corrosion

Water plays a central role in electrochemical corrosion by acting as the medium for ion transport and electron exchange. In conventional systems, corrosion is assumed to require a continuous aqueous phase. However, in gas-dominated or low-water multiphase systems, corrosion can still occur through thin-film electrolytes and deliquescent layers formed under condensation or wetting conditions [12].

Even trace amounts of water can form adsorbed molecular layers on the pipe wall, especially at dew-point temperatures. These microfilms, though invisible macroscopically, can sustain localized anodic and cathodic reactions by dissolving  $\text{CO}_2$  and enabling the carbonic acid chemistry described earlier. The phenomenon is referred to as **film-limited corrosion** and is especially dangerous because it may go undetected by bulk-phase water sensors [13].

Under certain conditions, hygroscopic salts or corrosion products may also absorb moisture from the gas phase, creating deliquescent brines that maintain electrolyte conductivity. These micro-environments allow corrosion to proceed intermittently, leading to **localized pitting** even in nominally dry segments. The corrosion rate in such regions is often underestimated by conventional models that rely solely on bulk water content [14].

The deliquescence threshold of salts such as  $\text{FeCl}_2$  or  $\text{CaCl}_2$  plays a determining role in this process. Once relative humidity exceeds this threshold, thin electrolyte layers form spontaneously. These brine films support high ionic mobility and localized acidity, both of which exacerbate metal dissolution [15].



**Figure 1** Schematic of  $\text{CO}_2$  corrosion mechanism under varying water contents

The schematic in Figure 1 illustrates the evolution of corrosion processes across different water regimes—from dry gas with no corrosion, to thin-film corrosion zones, and finally to full immersion scenarios. It also shows the interactions between flow dynamics, droplet behavior, and corrosion cell formation.

Recognizing the role of sub-visible water layers enhances the predictive accuracy of corrosion models, especially for high-pressure gas pipelines where conventional assumptions about aqueous corrosion may no longer apply. This insight has important implications for inhibitor deployment, inspection timing, and material selection.

## 3. Flow regimes and their effect on corrosion

### 3.1. Multiphase Flow Regimes in Pipelines

Multiphase flow in pipelines refers to the simultaneous movement of gas, liquid, and sometimes solid phases. The distribution of these phases results in different **flow regimes**, each exerting a unique influence on internal corrosion due to its impact on wetting behavior, phase separation, and shear stress [11].

One common regime is stratified flow, where gas flows above a liquid layer, separated by a stable interface. This regime typically occurs at low velocities and in horizontal pipelines. Corrosion is often limited to the bottom of the pipe, where the liquid resides, creating a risk of localized attack in the lower quadrant of the cross-section [12].

In slug flow, large liquid slugs interspersed with gas pockets move intermittently through the pipeline. The alternating exposure of the pipe wall to liquid and gas enhances oxygen and CO<sub>2</sub> mass transfer, which increases corrosion potential. Slug flow also causes mechanical stripping of protective films, exacerbating metal loss [13].

Annular flow occurs when gas flows in the center of the pipe while a thin liquid film coats the walls. This regime is typical at high velocities and is particularly critical from a corrosion standpoint, as the thin film may be insufficiently protective while still enabling electrolyte contact [14].

Mist flow represents the highest velocity regime, where the liquid phase exists as entrained droplets in a dominant gas stream. Though the pipeline appears dry, corrosion can still proceed via droplet deposition and localized wetting, particularly in the presence of CO<sub>2</sub> and hygroscopic salts [15].

Each regime presents different challenges for corrosion modeling and mitigation. Understanding the dynamic transitions between these regimes along pipeline segments is essential for predicting where water accumulates, film ruptures, or protective layers are eroded—each being a precursor to localized attack.

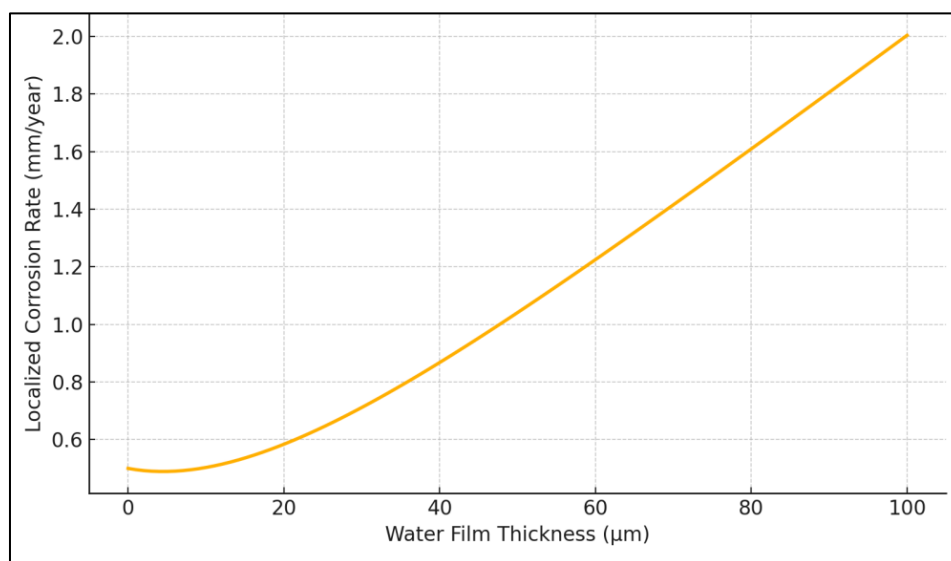
### 3.2. Film Wetting vs. Droplet Wetting and Corrosion Behavior

The mode of water contact with the pipe wall—either as a continuous film or discrete droplets—has significant implications for corrosion severity. In multiphase pipeline systems, this wetting behavior is dictated by flow regime, temperature, and wall energy conditions [16].

Film wetting refers to a uniform, continuous water layer that coats the internal surface of the pipeline. This condition is more likely in stratified or annular flows, where gravitational or inertial forces promote water phase adhesion. A continuous film enables steady-state electrochemical reactions, leading to generalized wall thinning. Depending on flow shear, this film may be thick or thin, but it often supports stable corrosion cell formation across a large area [17].

In contrast, droplet wetting involves the intermittent or patchy presence of water on the wall, as observed in mist or transitional flow regimes. Droplets deposit irregularly due to turbulence or condensation and result in localized corrosion cells, where anodic and cathodic reactions are spatially confined. The surrounding dry surface impedes electron flow, concentrating reactions at discrete sites and increasing pitting susceptibility [18].

The distinction between film and droplet wetting is critical because corrosion mitigation strategies often rely on assumptions of full-wall contact. In reality, areas with droplet wetting may be overlooked or underprotected, especially by inhibitors that require a continuous aqueous phase to function effectively [19].



**Figure 2** Correlation between Water Film Thickness and Localized Corrosion Rate

Figure 2 demonstrates that as water film thickness decreases to below a threshold (typically <50 microns), localized corrosion rates spike due to enhanced oxygen or CO<sub>2</sub> access and unstable inhibitor coverage. This explains why pipelines assumed to be “dry” based on water cut measurements can still experience severe localized attack.

By recognizing the difference between wetting modes, operators can fine-tune inspection strategies and adjust inhibitor concentrations or formulations to address these microenvironmental risks.

### 3.3. Localized Attack in Intermittently Wet Regions

Localized corrosion, including pitting and under-deposit corrosion, is increasingly reported in intermittently wet pipeline zones, particularly under CO<sub>2</sub>-rich environments where water is present in minimal but reactive quantities. These regions exist in flow conditions where water does not form a bulk phase but instead adheres as microfilms or deposits intermittently due to condensation or turbulence [20].

In such settings, pitting corrosion is driven by localized electrochemical gradients and the inability of corrosion products or inhibitors to form uniform, protective films. CO<sub>2</sub> lowers the pH of the water phase and supports the formation of carbonic acid, which aggressively attacks steel surfaces. When the water is present only intermittently, corrosion products such as FeCO<sub>3</sub> may not form a stable barrier, leaving fresh metal exposed during each wetting cycle [21].

Under-deposit corrosion emerges when solid particles—like sand, scale, or corrosion debris—settle on intermittently wet surfaces. These deposits create differential aeration cells beneath them, where oxygen or CO<sub>2</sub> concentration varies between the covered and uncovered zones. The covered region becomes anodic, accelerating corrosion beneath the deposit while masking it from external observation [22].

This form of localized attack is highly insidious and can result in deep wall penetration even when average corrosion rates remain low. The risk increases in mist or slug regimes, where flow irregularities and shear stress facilitate both droplet formation and particulate deposition.

**Table 1** Comparison of Corrosion Severity Across Flow Regimes with Low Water Presence

Flow Regime	Water Phase Behavior	Corrosion Severity	Dominant Mode
Stratified	Continuous at bottom	Moderate	Generalized
Slug	Intermittent slugs	High	Pitting, Film Disruption
Annular	Thin wall film	Variable	Wall Thinning
Mist	Droplet deposition	Severe (localized)	Pitting, Under-deposit

Localized corrosion in these regimes challenges standard monitoring methods and calls for **enhanced spatial resolution** in inspection technologies. Predictive models must integrate droplet dynamics and deposit behavior to improve risk assessment and mitigation strategies in these low-water yet high-risk environments [23].

## 4. Experimental investigations and modeling approaches

### 4.1. High-Pressure, Low-Water Laboratory Studies

To investigate the corrosion behavior of pipelines under low-water, CO<sub>2</sub>-rich conditions, several high-pressure laboratory experiments have been conducted using both static autoclaves and dynamic loop systems. These studies simulate multiphase pipeline environments with partial water saturation, allowing controlled evaluation of corrosion rates, wetting dynamics, and protective scale formation [15].

Static autoclave tests involve sealed reactors pressurized with CO<sub>2</sub> gas and introduced with a limited amount of water to mimic thin-film conditions. Carbon steel specimens placed within the autoclave are monitored over varying exposure durations and temperatures. Results consistently demonstrate measurable corrosion even at water cuts below 1%, validating the concept that visible bulk water is not required for electrochemical degradation. At 80–120°C, corrosion rates ranged from 0.1 to 0.7 mm/year depending on gas velocity and water film adhesion [16].

Visual inspection and surface analysis techniques such as SEM and EDX reveal pitting morphology on specimen surfaces. In many cases, localized corrosion spots correspond to regions of condensate accumulation, highlighting the effect of vapor-phase wetting. The presence of corrosion products—primarily iron carbonate ( $\text{FeCO}_3$ )—is noted, although the films formed under these low-water conditions are often porous and non-uniform [17].

Loop flow tests extend these findings by simulating actual multiphase flow in horizontal pipelines. These systems incorporate flow velocity, inclination, and temperature controls to replicate field conditions more closely. In  $\text{CO}_2$ -saturated environments, short bursts of wet gas flow—combined with wall condensation—have been observed to generate episodic pitting, consistent with field reports of under-deposit corrosion. Intermittent wetting triggers localized attack, with accelerated metal loss in impacted zones [18].

Collectively, these laboratory studies confirm that  $\text{CO}_2$  corrosion can occur even in marginally wet pipelines, especially under high-pressure conditions where water solubility in the gas phase enables thin-film or droplet formation. The implication is that standard water cut thresholds may underestimate corrosion risks, particularly in dry gas pipelines operating near condensation points. Understanding the limits of such thresholds is essential for redefining inspection intervals and inhibitor dosage strategies in dry-appearing but reactive systems [19].

#### 4.2. Thermodynamic Modeling of Scale Stability

Iron carbonate ( $\text{FeCO}_3$ ) scale formation is a key protective mechanism in  $\text{CO}_2$  corrosion systems. Under specific thermodynamic conditions,  $\text{Fe}^{2+}$  ions released by corrosion combine with carbonate ions in solution to form a precipitate on the metal surface. This precipitate acts as a barrier layer, reducing diffusion of corrosive species to the metal substrate. The stability of this layer can be assessed using the solubility product ( $K_{sp}$ ):

. Solubility Product Equation ( $\text{FeCO}_3$  Precipitation):

$$K_{sp} = [\text{Fe}^{2+}] [\text{CO}_3^{2-}]$$

Where:

- $K_{sp}$  is the solubility product constant of iron carbonate.
- $[\text{Fe}^{2+}]$  is the molar concentration of ferrous ions in solution.
- $[\text{CO}_3^{2-}]$  is the molar concentration of carbonate ions in solution.
- Precipitation of  $\text{FeCO}_3$  occurs when the product exceeds the  $K_{sp}$  value.

This expression indicates that precipitation occurs when the product of the ion concentrations exceeds the solubility limit, creating a supersaturated solution [20]. In practice, this is influenced by pH, temperature,  $\text{CO}_2$  partial pressure, and fluid composition. At moderate temperatures (around 60–80°C) and  $\text{pH} > 6.3$ ,  $\text{FeCO}_3$  tends to precipitate, provided that  $\text{Fe}^{2+}$  and  $\text{CO}_3^{2-}$  concentrations are maintained above saturation levels [21].

Thermodynamic modeling tools, such as OLI Studio and PHREEQC, simulate these interactions under varying pipeline conditions. Models show that increasing  $\text{CO}_2$  partial pressure lowers pH, which initially promotes corrosion by increasing  $\text{Fe}^{2+}$  dissolution. However, over time, elevated  $\text{Fe}^{2+}$  levels and buffering from bicarbonate lead to local supersaturation, initiating scale formation [22].

Temperature plays a dual role—raising both corrosion rate and scale precipitation rate. This results in a **nonlinear relationship**, where corrosion first accelerates, then decelerates as scale builds up. Modeling scenarios show that in environments with intermittent wetting, scale formation is hindered due to fluctuating saturation levels and insufficient residence time for nucleation and growth [23].

Furthermore, scale stability depends on **shear stress** and flow regime. In turbulent or slug flow, protective films are prone to erosion, particularly in elbows, reducers, and high-velocity segments. Thermodynamic models help map regions where stable scale is likely to persist versus areas at risk of mechanical film disruption.

Overall, incorporating solubility dynamics into corrosion prediction enhances the accuracy of life-cycle assessments and informs inhibitor selection by identifying zones where natural scale protection may suffice and where chemical intervention is required.

### 4.3. Kinetic Modeling of Localized Corrosion Events

While thermodynamic models explain *if* corrosion or scaling will occur, kinetic models provide insight into *how fast* localized degradation progresses, particularly under transient wetting conditions. In thin water film environments, corrosion kinetics become highly variable, driven by rapid changes in ion concentration, pH, and film disruption.

Localized corrosion begins when droplets or condensate form on the pipe wall, creating micro-environments conducive to electrochemical reactions. The corrosion rate in these zones is a function of time-dependent availability of water and CO<sub>2</sub>, as well as reaction surface area and electron transfer rates. Kinetic modeling uses these parameters to predict short-term metal loss, crucial for evaluating pitting potential [24].

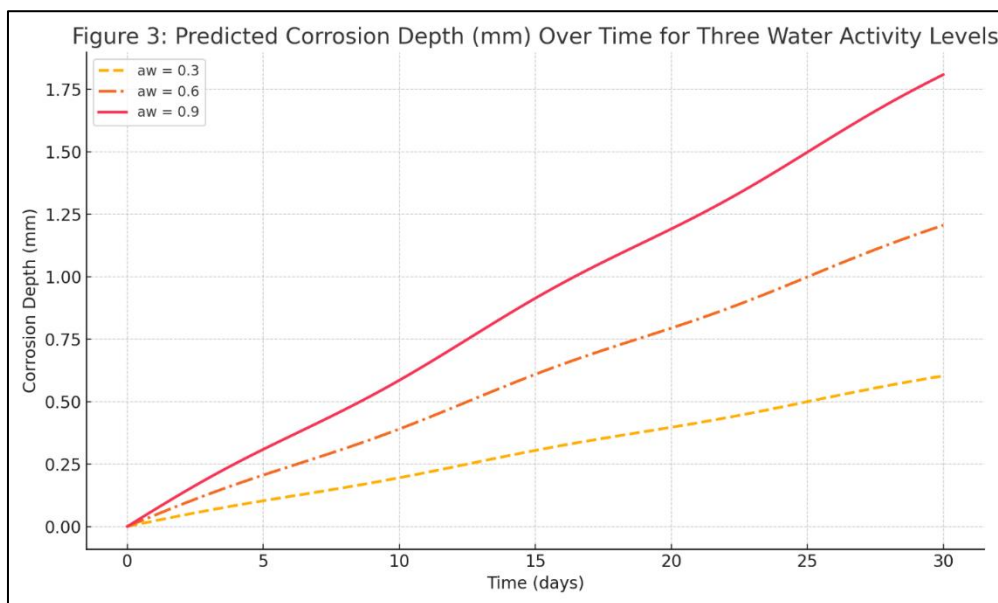
The governing equation includes electrochemical rate laws modified for thin films, accounting for restricted ion transport and limited buffering capacity. The rate of Fe dissolution, Localized Corrosion Rate Equation under Thin-Film Conditions:

$$r_{\text{Fe}} = k_{\text{corr}} \times [\text{H}^+]^n$$

Where:

- $r_{\text{Fe}}$  is the corrosion rate of iron (e.g., mm/year).
- $k_{\text{corr}}$  is the reaction rate constant specific to system conditions.
- $[\text{H}^+]$  is the hydrogen ion concentration.
- $n$  is the reaction order with respect to pH (usually between 1 and 2).
- This equation estimates short-term metal loss under acidic, film-limited corrosion environments.

Thin films concentrate reactants, amplifying the localized corrosion rate compared to fully immersed conditions.



**Figure 3** Predicted Corrosion Depth (mm) Over Time for Three Water Activity Levels

Figure 3 illustrates modeled corrosion depth versus time for three levels of water activity ( $aw = 0.3, 0.6, 0.9$ ). The results show that even at low water activity, corrosion initiates quickly and progresses faster during the first 24–48 hours, particularly in systems with high CO<sub>2</sub> partial pressures. These bursts of localized damage, although brief, contribute disproportionately to long-term risk due to their concentrated nature [25].

Kinetic simulations also reveal that protective scale cannot form fast enough under transient wetting, especially if the water film evaporates or is swept away before saturation is reached. This helps explain why pitting is often observed in field sections subjected to intermittent condensation or where liquid hold-up is minimal but variable.



Integrating kinetic models into digital twin systems enables near-real-time tracking of localized corrosion events and supports dynamic risk scoring. These tools allow pipeline operators to assess **immediate vulnerability** rather than relying solely on average corrosion rates, improving the precision of maintenance decisions and inhibitor deployment [26].

## 5. Effects of pressure, temperature, and gas composition

### 5.1. Pressure Influence on CO<sub>2</sub> Solubility and Acidity

Pressure plays a critical role in determining the solubility of carbon dioxide in pipeline fluids, directly influencing the acidity and corrosiveness of the environment. In multiphase oil and gas systems, increased pressure enhances the dissolution of CO<sub>2</sub> into the aqueous phase according to **Henry's Law**:

Henry's Law for CO<sub>2</sub> Solubility:

$$C_{\text{CO}_2} = k_H \times P_{\text{CO}_2}$$

Where:

- $C_{\text{CO}_2}$  is the concentration of dissolved carbon dioxide (mol/L).
- $k_H$  is Henry's constant (mol/(L·atm)), which depends on temperature.
- $P_{\text{CO}_2}$  is the partial pressure of CO<sub>2</sub> (atm).

This equation expresses that the solubility of CO<sub>2</sub> in a liquid is directly proportional to its partial pressure in the gas phase. This, in turn, leads to greater formation of carbonic acid, which lowers the pH of the aqueous phase and increases the potential for internal corrosion [20].

In high-pressure gas pipelines or deepwater transmission lines, partial CO<sub>2</sub> pressures can exceed several bars, substantially increasing CO<sub>2</sub> loading. Laboratory studies show that at pressures above 10 bar, pH can drop below 4.5 even with relatively low water content. This acidic environment is highly conducive to general and localized corrosion, especially where protective scales like FeCO<sub>3</sub> have not yet formed or are unstable [21].

Moreover, high-pressure environments support microfilm formation through CO<sub>2</sub> condensation or deliquescence, making even "dry" segments susceptible to corrosion initiation. Pressure-induced solubility also affects the behavior of corrosion inhibitors, as elevated CO<sub>2</sub> loading may neutralize weak-base inhibitors or affect their partitioning at the gas-liquid interface [22].

Therefore, accurate modeling of CO<sub>2</sub> solubility under operating pressure conditions is essential for predicting pH profiles, corrosion risks, and inhibitor demand. Pipeline segments operating at elevated pressures should be prioritized for enhanced monitoring and modeled with time-varying solubility dynamics to reflect their greater sensitivity to flow rate changes and condensation phenomena [23].

### 5.2. Temperature and Its Dual Effect on Solubility and Kinetics

Temperature exerts a dual and often competing influence on CO<sub>2</sub> corrosion in pipelines by simultaneously affecting solubility behavior and corrosion reaction kinetics. As temperature increases, the solubility of CO<sub>2</sub> in water decreases due to the exothermic nature of gas dissolution. However, corrosion kinetics accelerate with temperature due to enhanced electrochemical activity and faster mass transport [24].

This means that in moderately heated pipeline environments (40–80°C), there is often a trade-off between reduced CO<sub>2</sub> availability and increased metal reactivity. Although less CO<sub>2</sub> dissolves, the corrosion rate may still rise because the activation energy barrier for anodic dissolution and cathodic hydrogen evolution is lowered. Electrochemical testing confirms that steel corrosion rates can nearly double when temperature increases from 40°C to 70°C under constant CO<sub>2</sub> partial pressure [25].

Higher temperatures also influence scale formation—particularly the precipitation of FeCO<sub>3</sub>. As temperature increases, the saturation index of iron carbonate rises, facilitating nucleation and growth of protective scale. In fact, FeCO<sub>3</sub>

solubility decreases with temperature, favoring precipitation. This effect helps mitigate corrosion if scale adheres firmly to the pipe wall and remains undisturbed by flow [26].

However, temperature-driven precipitation is not always beneficial. In systems with high flow turbulence or slugging, the scale may be mechanically eroded, reducing its effectiveness. Moreover, at elevated temperatures, inhibitor degradation becomes a concern. Some organic inhibitors lose functionality or decompose, requiring careful selection or higher dosage to remain effective [27].

The net outcome of temperature effects depends on flow regime, water chemistry, and pipeline material. In general, corrosion risk is highest at intermediate temperatures (60–80°C), where reaction rates are high and stable scale formation may not yet occur. Hence, thermally sensitive pipeline segments require condition-specific modeling and mitigation strategies that balance kinetic acceleration with thermodynamic scaling potential [28].

### 5.3. Interplay with Hydrocarbon Composition

The type and composition of hydrocarbon flowing in a pipeline—whether light gas condensates or heavier crude oils—influences corrosion behavior by affecting water transport, wetting dynamics, and phase interaction. Hydrocarbon phase properties determine how water is dispersed, transported, and deposited along the pipeline wall [29].

In light hydrocarbon systems, such as natural gas or condensate pipelines, water typically exists as a separate phase or fine mist. These systems are more prone to droplet deposition and intermittent wetting, particularly under high-velocity or annular flow conditions. This increases the likelihood of localized corrosion and under-deposit pitting in regions where droplets accumulate and form electrolyte microenvironments [30].

In contrast, heavy crude oils may entrain water more effectively, forming stable emulsions that can reduce droplet formation and limit wall contact. However, this does not eliminate corrosion risk. Instead, emulsified systems may lead to under-emulsion corrosion, where water droplets become trapped beneath an oil layer at the steel interface. These isolated zones can exhibit low oxygen concentration and high ionic activity, creating corrosive cells with poor inhibitor accessibility [31].

Additionally, heavier hydrocarbons carry more organic acids and sulfur compounds, which may exacerbate corrosion or interact with inhibitors. The chemical composition influences not just corrosion rate but also scale composition, with asphaltenes and other organics potentially interfering with  $\text{FeCO}_3$  nucleation and film adherence.

**Table 2** Summary of Environmental Condition Influence on Corrosion Rate

Condition	Corrosion Impact
High $\text{CO}_2$ Partial Pressure	Increased acidity, faster initiation
Elevated Temperature	Higher kinetics, enhanced scaling
Light Hydrocarbon Flow	More droplet wetting, localized attack
Heavy Crude Flow	Emulsion formation, complex interfaces
High Turbulence/Slug Flow	Film erosion, inhibitor breakdown

Understanding the combined effect of these variables is critical for tailoring corrosion prediction models and mitigation programs to the fluid properties of each pipeline segment [32].

## 6. Iron carbonate scale behavior under low-water conditions

### 6.1. Conditions for Protective vs. Non-Protective Scale

The formation of iron carbonate ( $\text{FeCO}_3$ ) scale is a key determinant in the progression or inhibition of  $\text{CO}_2$ -induced corrosion in carbon steel pipelines. Whether this scale acts as a protective barrier or fails to mitigate corrosion depends largely on the conditions governing its nucleation, growth, and stability [23].

A primary metric for assessing scale-forming potential is the supersaturation index (SI), defined as the ratio of the ion activity product to the solubility product ( $\text{K}_{\text{sp}}K_{\text{sp}}$ ) of  $\text{FeCO}_3$ . Supersaturation occurs when the product of  $\text{Fe}^{2+}$

and  $\text{CO}_3^{2-}$  concentrations exceeds  $K_{sp}$ , making precipitation thermodynamically favorable. A higher SI indicates a greater driving force for nucleation and faster growth rates [24].

Temperature has a dual influence. It decreases  $\text{FeCO}_3$  solubility, thereby promoting precipitation, and also accelerates corrosion kinetics, which increases  $\text{Fe}^{2+}$  concentration in the fluid. This coupling often leads to early formation of scale at moderate to high temperatures (60–90°C), provided that carbonate ions are not limiting [25]. However, in systems with low alkalinity or buffering capacity, carbonate availability may lag behind  $\text{Fe}^{2+}$  production, delaying the onset of precipitation and leaving the metal surface vulnerable.

Nucleation kinetics are also vital. The presence of solid interfaces, micro-roughness, or corrosion products can act as nucleation sites. Once nucleated,  $\text{FeCO}_3$  scale must grow to a critical thickness and crystallinity to reduce porosity and become protective. Incomplete or amorphous layers remain permeable to corrosive species and may even concentrate corrosion under differential aeration conditions [26].

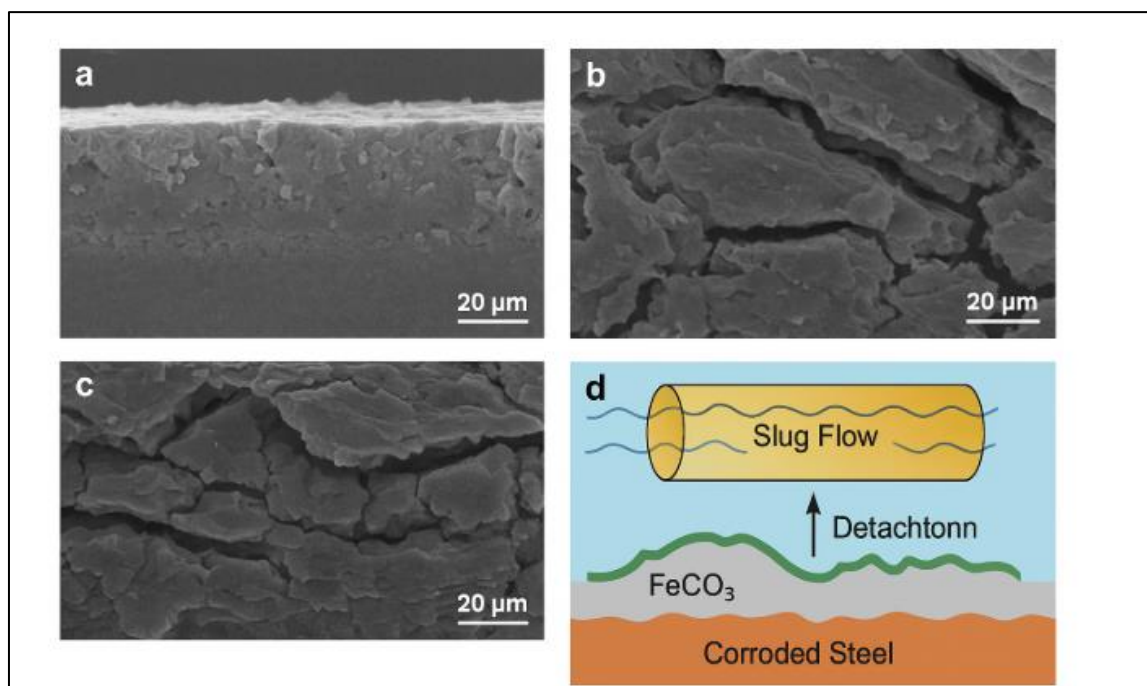
Protective behavior also depends on adherence and coverage. Uniform, dense, and adherent  $\text{FeCO}_3$  layers block ion transport and suppress further corrosion. In contrast, **non-protective scales**—often observed in dynamic flow or under low saturation—are patchy and friable. These fail to form a continuous barrier and may spall under mechanical or chemical stress.

Recognizing the precise threshold where protective behavior transitions to non-protective is critical for predictive corrosion modeling. Operators must evaluate SI, flow conditions, and fluid chemistry to determine where  $\text{FeCO}_3$  formation may be sufficient for protection and where it may require chemical augmentation or flow adjustment [27].

## 6.2. Degradation of $\text{FeCO}_3$ Scale at High Shear Zones

Even when  $\text{FeCO}_3$  forms under favorable thermodynamic conditions, its mechanical stability can be compromised in high shear regions of the pipeline. These zones, such as elbows, reducers, or sections experiencing slug flow, exert strong wall shear stress and turbulence, which challenge the integrity of scale layers [28].

In slug flow, alternating slugs of liquid and gas exert pulsating hydrodynamic forces on the pipe wall. These forces cause repeated mechanical impact and shear, which can erode or delaminate even well-crystallized  $\text{FeCO}_3$  films. High-resolution surface characterization, such as scanning electron microscopy (SEM), reveals that the  $\text{FeCO}_3$  surface in such areas becomes cracked, pitted, or completely stripped over time [29].



**Figure 4** SEM Images or Schematic of  $\text{FeCO}_3$  Layer Breakdown in Slug Flow [22]

Figure 4 illustrates how the initially uniform scale develops microfractures and loses cohesion under cyclic flow. These disruptions not only expose bare metal to corrosive fluid but also interfere with repassivation by preventing uniform ion transport and buffering at the steel surface [30].

Furthermore, once the scale is partially removed, differential flow velocities along the surface create zones of turbulence and stagnation, leading to irregular corrosion cell development. In high-shear zones, reformation of  $\text{FeCO}_3$  is often slow, especially if the system operates near the threshold of saturation or has insufficient residence time for nucleation.

Inhibitor performance is also affected. Organic inhibitors may not adsorb effectively in regions where  $\text{FeCO}_3$  is patchy, and they may be swept away by turbulent bursts. Therefore, high shear environments require enhanced inhibitor dosing, alternative scale chemistries, or flow modification to mitigate the risk of scale degradation and local corrosion propagation [31].

### 6.3. Impact of Flow Cycling and $\text{CO}_2$ Saturation Fluctuation

Flow cycling, common in batch operations or fluctuating production wells, induces transient changes in pressure, temperature, and fluid composition that destabilize  $\text{FeCO}_3$  scale and affect corrosion dynamics. During low-flow or shutdown periods,  $\text{CO}_2$  levels near the wall may rise due to diffusion and condensation, increasing local acidity and initiating scale dissolution [32].

When flow resumes, the sudden influx of undersaturated fluid may fail to immediately re-establish the supersaturation required for  $\text{FeCO}_3$  precipitation. This lag period—referred to as the repassivation delay—allows active corrosion to occur on exposed steel until saturation and nucleation conditions are reattained. Repassivation delays of several hours have been documented in lab simulations, particularly when  $\text{CO}_2$  levels fluctuate by more than 20% [33].

$\text{CO}_2$  saturation also controls the stability of existing scale layers. A drop in  $\text{CO}_2$  partial pressure reduces bicarbonate and carbonate concentrations, potentially undersaturating the environment and initiating scale dissolution. This makes scale layers vulnerable to thinning or partial delamination, especially in less-protected pipeline segments.

Moreover, cycling affects water film behavior. During shutdowns, water may settle or stratify, altering wetting profiles and promoting uneven corrosion. Upon startup, re-entrained water may carry particulates that abrade recovering scale, compounding the repassivation challenge.

These transient conditions are not always captured in steady-state corrosion models, leading to underestimation of peak risk events. To mitigate these effects, systems with frequent flow interruptions require dynamic modeling, robust inhibitor systems capable of rapid adsorption, and strategic use of sacrificial anodes or alloy upgrades in high-risk segments [34].

By understanding how flow and saturation fluctuations impact corrosion behavior, operators can implement condition-specific protocols that reduce downtime-induced damage and prolong the integrity of both protective films and pipeline assets [35].

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## 7. Application to risk assessment and predictive models

### 7.1. Industry Models and Empirical Limitations

Empirical models have long served as foundational tools for estimating internal corrosion rates in  $\text{CO}_2$ -containing pipeline systems. Among the most widely used are the NORSOK M-506, de Waard–Milliams, and Electrochemical Corrosion Equation (ECE) models. These models provide industry practitioners with rapid assessment tools based on simplified assumptions and controlled datasets [19].

The de Waard–Milliams model, developed in the 1970s, estimates corrosion rates as a function of temperature and partial pressure of  $\text{CO}_2$ . While it remains popular due to its simplicity, its predictive accuracy is limited under dynamic flow, scale-forming environments, or varying water cuts. The model assumes a linear flow profile and homogeneous corrosion conditions, which often do not reflect real multiphase flow complexities [20].

NORSOK M-506, developed by the Norwegian petroleum industry, extends empirical modeling by incorporating pH, bicarbonate concentration, and  $\text{Fe}^{2+}$  ion content into its framework. It offers better coverage across operating scenarios,

yet still relies on assumptions about static flow and full wettability, neglecting the intermittent and localized wetting common in gas-dominant systems [21].

The ECE model incorporates some electrochemical aspects, such as hydrogen evolution and mass transport limitations. However, it remains semi-empirical and poorly accounts for surface heterogeneity or scale behavior. As a result, discrepancies between predicted and observed corrosion rates persist, especially in high-shear, low-water, or condensate-rich environments [22].

While these models provide valuable initial estimates, their inability to resolve localized phenomena such as pitting or under-deposit corrosion limits their use for risk-informed design. They also struggle to adapt to real-time data inputs or integrate with sensor-based digital monitoring. Consequently, the industry is shifting toward hybrid frameworks that combine empirical baselines with data-driven corrections or mechanistic enhancements to overcome the empirical rigidity of legacy models [23].

## 7.2. Data-Driven Improvements and CFD Simulations

To address the shortcomings of empirical models, the industry is increasingly adopting data-driven and computational approaches to enhance corrosion prediction accuracy. Machine learning (ML) and Computational Fluid Dynamics (CFD) are at the forefront of this transition, enabling spatially resolved, adaptive modeling of corrosion behavior in complex pipeline systems [24].

CFD simulations allow for detailed visualization of flow regimes, shear stress distribution, droplet impact zones, and condensation points, which are all critical parameters in determining localized corrosion risk. Unlike empirical models, CFD can simulate multiphase interactions and wall wetting behavior under transient operating conditions. However, CFD alone does not predict corrosion rates—it offers input conditions and flow characteristics that must be coupled with chemical and material degradation models [25].

Machine learning models such as Random Forest, Support Vector Machines (SVM), and Gradient Boosting Machines (GBM) can ingest large volumes of historical inspection data, environmental readings, and sensor outputs to identify patterns associated with corrosion initiation and progression. These models excel in handling nonlinear relationships and are particularly valuable for anomaly detection in sensor-based digital twin platforms [26].

The most promising approach combines CFD output as features into ML frameworks—creating hybrid models that use physics-informed CFD data to train AI systems in recognizing corrosion hotspots. These models can dynamically update based on real-time inputs and field data, continuously refining predictions and improving accuracy over time [27].

By leveraging CFD's spatial precision and ML's predictive power, operators can move beyond average corrosion estimates toward location-specific risk profiling. This hybrid methodology supports smarter inspection planning, predictive maintenance, and optimization of chemical treatment strategies across variable pipeline conditions.

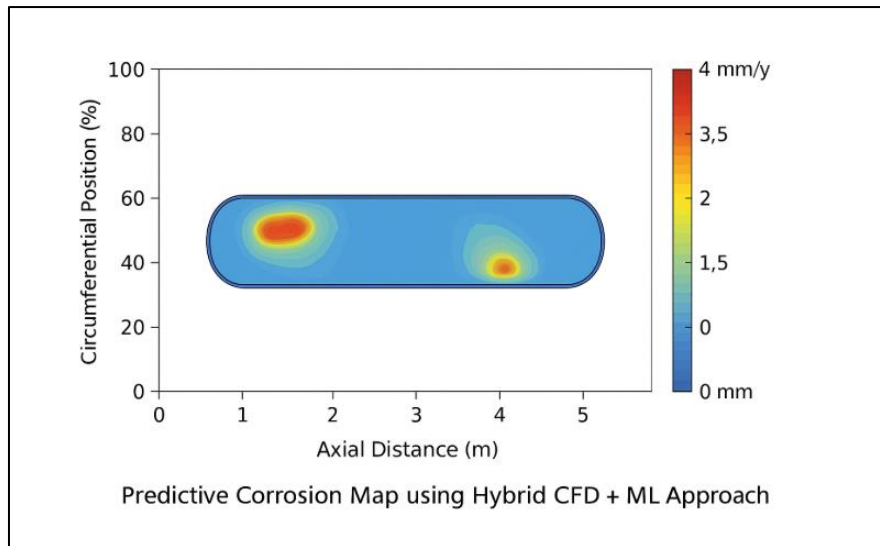
## 7.3. Integrating Predictive Models into Pipeline Design

The integration of predictive corrosion models into pipeline design processes represents a transformative step toward proactive integrity management. Unlike post-construction monitoring, model-informed design embeds risk mitigation into the engineering lifecycle, ensuring that material selection, wall thickness, and flow regime choices are informed by anticipated degradation patterns [28].

Modern pipeline design tools now incorporate hybrid corrosion models that combine mechanistic frameworks with CFD-informed simulations. These platforms allow engineers to simulate operational conditions—temperature, pressure, velocity, and composition—along the pipeline length and generate predictive maps of corrosion intensity.

Figure 5 shows an example corrosion map generated by such an integrated model, highlighting zones of elevated risk due to shear stress amplification, CO<sub>2</sub> condensation, or intermittent wetting. This visual guide supports the targeted application of corrosion allowances or protective coatings during the design phase, reducing lifecycle costs and inspection burdens later on [29].

Moreover, predictive modeling aids in intelligent sensor placement. By forecasting where corrosion is most likely to occur, designers can deploy monitoring equipment precisely, improving detection response and data quality. This is especially important in subsea or inaccessible segments, where over-monitoring is impractical and under-monitoring is risky.



**Figure 5** Predictive Corrosion Map Using Hybrid CFD + ML Approach

**Table 3** Model Comparison Summary: Empirical, Mechanistic, and Hybrid Approaches

Model Type	Advantages	Limitations
Empirical	Fast, easy to apply	Poor spatial resolution, static input
Mechanistic	Physically grounded, semi-dynamic	Computationally intensive, requires tuning
Hybrid (CFD + ML)	High accuracy, adaptive, spatially rich	High setup complexity, data-dependent

By embedding these models within digital design workflows, the industry can align integrity forecasting with operational and financial planning. This approach represents a shift from reactive pipeline integrity to risk-informed infrastructure engineering, enabling smarter investments and safer energy transport [30].

## 8. Implications for corrosion mitigation strategy

### 8.1. Chemical Inhibitor Application in Low-Water Systems

In multiphase pipelines where water content is minimal, conventional corrosion inhibitors face significant limitations. These environments challenge both inhibitor transport and adsorption, prompting a need for specialized chemical formulations and carefully timed deployment strategies. In low-water systems, corrosion often arises from transient wetting events such as droplet deposition or condensation, which create thin electrolyte films conducive to localized attack [23].

Surfactant-based film-forming inhibitors are one of the most effective strategies under such conditions. These inhibitors possess amphiphilic structures that allow them to adhere to the steel surface in the absence of bulk water. Once adsorbed, they form a hydrophobic barrier that impedes access of corrosive species such as  $\text{CO}_2$  and  $\text{H}^+$  ions. Their low water dependency and high surface affinity make them ideal for annular and mist flow regimes [24].

Vapor-phase corrosion inhibitors (VCIs) offer an additional layer of protection by volatilizing into the gas stream and adsorbing onto exposed metal surfaces. These are particularly useful during shutdowns or low-flow periods when moisture condenses on pipe walls. VCIs can also be introduced during commissioning or pigging operations to provide baseline protection during dry startup phases [25].

Timing of deployment is critical. Inhibitors must be introduced when there is sufficient film or moisture presence to facilitate transport and adsorption. If injected too early or too late, inhibitors may either be swept away or fail to reach vulnerable regions. Strategies such as batch injection timed with slug flow intervals, or continuous low-dose injection tuned to flow conditions, are commonly used to enhance effectiveness [26].

Optimization of chemical strategy in low-water systems requires fluid dynamics modeling, historical failure data, and validation through field testing. With precise application, chemical inhibitors can reduce corrosion significantly even in environments previously considered marginally reactive.

## 8.2. Role of Pipeline Design and Drainage Management

Effective pipeline design can greatly influence corrosion risk by managing the frequency, duration, and severity of wetting conditions. In low-water CO<sub>2</sub> environments, the corrosion threat is closely tied to fluid behavior—particularly the formation and persistence of water films following condensation, slug flow, or mist deposition. Design modifications that reduce liquid hold-up or facilitate drainage can minimize the presence of these corrosive microfilms [27].

One of the most influential parameters is slug frequency. Frequent slugs not only deliver water to the pipe wall but also strip away protective inhibitor films, exacerbating corrosion. Pipeline inclination, diameter, and flow velocity directly affect slug dynamics. Flow assurance modeling during the design phase allows engineers to optimize line profiles, reduce transition zones, and stabilize flow regimes to mitigate intermittent wetting [28].

Another critical aspect is drainage management, particularly in horizontal or inclined lines. Poor drainage can result in localized water pooling or film accumulation, creating persistent corrosion cells. Designing for enhanced condensate removal through strategically placed low points, drain valves, and separator integration can significantly reduce wetting duration and frequency.

In subsea pipelines, dead legs and low-flow branches require special attention. These areas are prone to stagnant film retention and must be designed with bypasses, flushing capabilities, or sacrificial anode systems to limit exposure. By integrating drainage-focused considerations into pipeline design, operators can proactively reduce the likelihood of underfilm corrosion and extend system lifespan, especially in systems where chemical mitigation alone is insufficient [29].

## 8.3. Recommendations for Monitoring and Inspection

Given the hidden and intermittent nature of corrosion in low-water CO<sub>2</sub> pipeline systems, monitoring and inspection strategies must be tailored to detect early degradation with high spatial and temporal resolution. Conventional monitoring intervals may miss corrosion that occurs during brief wetting episodes; hence, continuous or near-real-time techniques are recommended [30].

Ultrasonic testing (UT) pigging remains one of the most reliable inspection methods for detecting internal corrosion. Modern UT pigs offer high-resolution wall thickness mapping and can detect localized thinning down to sub-millimeter precision. When deployed periodically in high-risk segments, UT pigs can verify the effectiveness of chemical programs and identify pitting trends along the pipe length [31].

For continuous monitoring, acoustic emission (AE) sensors provide non-intrusive detection of active corrosion events. These sensors capture stress waves generated by crack formation or hydrogen evolution, offering early warnings without requiring access to the fluid stream. AE monitoring is particularly useful in subsea or buried pipelines, where traditional inspection is costly and infrequent [32].

Another promising technique involves intelligent corrosion probes, which can measure electrical resistance or linear polarization resistance in localized zones. These probes are embedded into pipeline walls or retrievable coupons and provide real-time corrosion rate data. When placed in predicted wetting hotspots identified by flow or CFD models, they serve as critical feedback tools for dynamic inhibitor adjustment.

Integrating these tools into a centralized monitoring framework enables data-driven risk management, improves inspection targeting, and reduces both operational costs and unplanned downtime across complex pipeline networks [33].

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## 9. Conclusion

### 9.1. Key Insights

This study underscores that corrosion in pipeline systems is not confined to visibly wet or fully saturated environments. Instead, low-water, high-CO<sub>2</sub> conditions can still foster severe localized corrosion due to the presence of transient

wetting, thin water films, and hygroscopic salt formation. These microenvironments support electrochemical reactions, particularly in areas affected by mist, slug, or annular flow. Traditional corrosion models—which assume bulk water as a prerequisite—often underestimate this risk, leading to gaps in surveillance and delayed mitigation. The formation of non-uniform  $\text{FeCO}_3$  scales further complicates protection, especially in high-shear or unsteady flow conditions. This highlights the need for hybrid modeling that integrates flow dynamics, chemical equilibria, and surface wetting behaviors. Additionally, corrosion inhibitors can be effective in these systems, but their success depends on timing, surfactant properties, and compatibility with partial wetting zones. Overall, the findings emphasize a more nuanced understanding of flow-corrosion interactions in semi-dry pipeline environments.

## 9.2. Practical Recommendations

To mitigate corrosion under marginally wet conditions, operators should adopt flow-regime-specific models and align inspection schedules with dynamic risk maps derived from CFD and machine learning tools. Chemical inhibitor programs must be tailored for mist and slug flows, prioritizing surfactant-based or vapor-phase formulations. Pipeline designs should integrate drainage optimization, dead leg reduction, and sensor placement strategies based on predicted wetting zones. Continuous monitoring using UT pigging, intelligent probes, and acoustic systems ensures early detection. Above all, decision-making should be driven by integrated, predictive surveillance platforms capable of adapting to both operational variability and long-term corrosion behavior trends.

## 9.3. Future Research Needs

Further work is required to develop integrated experimental pipelines coupled with digital twin frameworks for semi-dry  $\text{CO}_2$  systems. These should simulate low-water, multiphase conditions in real-time to validate hybrid corrosion models, guide sensor placement, and support the evolution of AI-enhanced predictive maintenance in critical infrastructure.

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## Compliance with ethical standards

### *Disclosure of conflict of interest*

No conflict of interest to be disclosed.

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