

Field Corrosion Rates of Oilfield Carbon and Low-Alloy Steels across the Sweet-to-Sour (CO₂/H₂S) Spectrum: A Field Dataset and a Benchmark of Predictive Models

Soheyl Soleymani

RBI Clue Institute, Vancouver, Canada

Email: soheyl.soleymani@yahoo.com

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Abstract

Internal corrosion of carbon and low-alloy steels by dissolved carbon dioxide (CO₂) and hydrogen sulfide (H₂S) is a leading integrity threat in oil and gas production and transportation, yet field corrosion rates are rarely reported together with the quantified partial pressures that control them, which limits validation of engineering prediction models across the full sweet-to-sour range. This work compiles 90 field corrosion-rate measurements from operating oil and gas assets of an anonymous client operator, each paired with the steel grade, the operating temperature and pressure, the gas-phase CO₂ and H₂S contents, water chemistry, flow velocity and inhibitor status. Carbon dioxide and hydrogen sulfide partial pressures and *in-situ* pH were computed for every record, and each record was classified as sweet, mixed or sour from the pCO₂/pH₂S ratio. Measured rates ranged from 0.12 to 14.97 mm/yr (mean 2.29 mm/yr) and increased significantly with H₂S partial pressure ($r = +0.42$, $p < 0.001$) and with decreasing *in-situ* pH ($r = -0.49$, $p < 0.001$). Uninhibited general-corrosion records ($n = 27$) were benchmarked against the de Waard-Milliams 1991 model, its scale-corrected form, and a flow-coupled mass-transfer form. The uncorrected model over-predicted field rates by more than an order of magnitude (median measured/predicted ratio 0.05); the scale correction reduced but did not close the gap (median ratio 0.18; 11% of points within a factor of two), and the deviation depended systematically on service regime and H₂S partial pressure. The results provide an anonymized, openly described field dataset and quantify the limits of CO₂-only models in mixed and sour service.

Keywords

CO₂ Corrosion, H₂S, Sour Corrosion, API 5L, Pipeline Steel, de Waard-Milliams, Norsok M-506, Corrosion Rate, Field Data, Produced

1. Introduction

Internal corrosion driven by produced water and dissolved acid gases remains one of the most costly and safety-critical degradation modes in upstream and mid-stream oil and gas operations. Water co-produced with hydrocarbons carries a complex geochemical matrix and dissolved gases that attack carbon and low-alloy steels in pipelines, flowlines, downhole tubulars and separation equipment [1]. When operating conditions move outside the design envelope, the resulting wall loss and localized attack can lead to leaks and through-wall failures at preferential sites such as bends, weld joints and low points where water accumulates [2].

Carbon dioxide and hydrogen sulfide are the dominant internal corrosidents. In sweet service, dissolved CO_2 forms carbonic acid and drives general and localized corrosion whose severity depends strongly on CO_2 partial pressure, temperature and the stability of iron carbonate (FeCO_3) scale; in sour service, H_2S controls the surface chemistry through the formation of iron sulfide (FeS) films that can be either protective or locally damaging. Laboratory studies on line-pipe grades such as API 5L X52 confirm that, at elevated H_2S and CO_2 contents, iron sulfides dominate the corrosion product and the damage morphology shifts accordingly [3]. Engineering prediction of these rates has relied for decades on semi-empirical and analytical models: the de Waard-Milliams correlation relates corrosion rate to CO_2 partial pressure, temperature and pH; a flow-dependent extension couples the reaction rate to mass transfer through liquid velocity; and the NORSOK M-506 model adds wall shear stress and a temperature-dependent pH function. Semi-empirical and analytical corrosion-rate models of this kind have been developed and applied across a range of steel and process settings [4] [5]. Complementary mechanistic studies show how steel metallurgy and surface-film formation govern localized attack, and note that H_2S , protective scaling and flow strongly modify the response [6].

Despite the maturity of these models, field corrosion rates are seldom published alongside the quantified partial pressures and water chemistry needed to test them. Most field reports describe service qualitatively as sweet or sour, or quote laboratory exposures performed at gas saturation without stated partial pressures, so the inputs required by the engineering models cannot be reconstructed. Recent work has begun to infer corrosion rates from the dissolution of alloying constituents in produced water, providing rate estimates for dozens of wells, but still without the gas-phase partial pressures that govern the mechanism [7]. In parallel, data-driven and artificial-intelligence frameworks for corrosion-resistant material selection have been proposed, and these explicitly identify data scarcity, especially the absence of field datasets spanning a wide range of service conditions, as the main obstacle to progress [8].

Cracking-related damage in the same steels, including sulfide stress cracking and stress-corrosion cracking, has been documented in case studies of X52 ammonia pipelines [9] and in failure analyses of high-strength X70M line pipe [10], underscoring that the same environments that drive wall loss also raise cracking risk. The present study, however, focuses on quantifying general and localized wall-loss rates and on benchmarking the predictive models against measured field data. The objectives are: 1) to present an anonymized field corrosion-rate dataset for three common oilfield steels, each record paired with the operating drivers; 2) to map the data on the sweet-to-sour spectrum using computed CO_2 and H_2S partial pressures; and 3) to benchmark measured rates against the de Waard-Milliams family of models and quantify where, and by how much, the predictions deviate in mixed and sour service.

2. Sweet and Sour Corrosion and Predictive Models

In aqueous CO_2 service, the corrosion rate of carbon steel is governed by the partial pressure of CO_2 , temperature, solution pH and the formation of protective FeCO_3 scale. The de Waard-Milliams relationship expresses the baseline (worst-case, scale-free) corrosion rate as a function of temperature and CO_2 partial pressure. Above a temperature that depends on CO_2 partial pressure, FeCO_3 precipitates and forms a protective layer that sharply reduces the rate; this is represented by a scaling-temperature correction factor that lowers the predicted rate relative to the worst-case value. Flow influences the rate through mass transfer of corrosive species to, and corrosion products away from, the steel surface; the de Waard-Lotz-Dugstad model combines a reaction-controlled term with a velocity- and diameter-dependent mass-transfer term, while NORSOK M-506 expresses the flow effect through wall shear stress together with a temperature-dependent pH function. Analytical and semi-empirical corrosion models of this kind have been applied to steel equipment and structures in service [4] [5].

Hydrogen sulfide changes the picture qualitatively. Even at low partial pressures it can dominate surface chemistry through FeS formation, and the protectiveness of the sulfide film depends on the $\text{pCO}_2/\text{pH}_2\text{S}$ ratio, temperature and flow. None of the CO_2 -only engineering models above explicitly represents H_2S , so their accuracy in mixed and sour service is uncertain and must be established empirically; the role of steel metallurgy and surface films in setting localized attack further complicates a purely CO_2 -based description [6]. Temperature plays a dual role, accelerating reaction kinetics at low temperature but promoting protective scaling at higher temperature, an effect demonstrated for crude-distillation systems where corrosion factors peak and then decline with rising temperature [11]. Flow can be protective when it is smooth and aggressive when it is turbulent enough to disrupt protective layers, a transition captured by dimensionless-number analyses of flow-induced corrosion [12]. Finally, the intrinsic resistance of the base material varies with composition and microstructure across the ferrous alloys used in oilfield service [13]. The dataset assembled here was designed to span these drivers so that model performance could be evaluated across realistic conditions.

3. Materials and Methods

3.1. Field Dataset and Assets

The dataset comprises 90 corrosion-rate measurements collected from operating oil and gas assets of an anonymous client operator, including pipelines, flowlines, downhole tubing and separation equipment in sweet, mixed and sour service. All records are field data acquired from in-service equipment. Each record represents one corrosion-rate measurement at one location over a defined monitoring period, together with the operating conditions, water chemistry, flow and inhibitor status applicable to that same period. Operator, field and well identifiers have been removed and assets are referred to only by anonymized codes; see the Data Availability statement.

3.2. Steels

Three steels common in oilfield service are represented in equal numbers: two line-pipe grades, API 5L X52 (PSL2) and API 5L X65 (PSL2), and the carbon steel ASTM A106 Grade B. All are carbon or low-alloy steels relying on environmental control rather than intrinsic alloying for corrosion resistance.

3.3. Corrosion-Rate Measurement

Corrosion rates were obtained by established field and laboratory monitoring methods, comprising electrical-resistance (ER) and linear-polarization-resistance (LPR) probes, gravimetric weight-loss coupons and ultrasonic wall-thickness measurement. The measurement method, the rate basis (general or localized) and the exposure period are recorded for every point. General and localized (pitting) rates are kept distinct and are not averaged together. All rates were normalized to millimetres per year (mm/yr); where rates were reported in mils per year they were converted using $1 \text{ mpy} = 0.0254 \text{ mm/yr}$. For the inhibited-versus-uninhibited comparison reported in Section 4.7, only general-corrosion records were used, so that general and localized rates are never pooled.

3.4. Operating Conditions, Partial Pressures and pH

For each record, the operating temperature, total pressure, gas-phase CO_2 and H_2S contents, chloride, bicarbonate, flow velocity, pipe inner diameter and inhibitor status were compiled. Carbon dioxide and hydrogen sulfide partial pressures were computed as the product of the gas mole fraction and the total system pressure. *In-situ* pH was used as measured where available; otherwise it was estimated from the carbonic-acid equilibrium using the computed CO_2 partial pressure and the measured bicarbonate concentration. These computed quantities provide the inputs required by the predictive models.

3.5. Service-Regime Classification

Each record was classified by the ratio of CO_2 to H_2S partial pressure: sweet for

pCO₂/pH₂S greater than 500, mixed for ratios between 20 and 500, and sour for ratios below 20. This widely used partitioning reflects the transition from FeCO₃-dominated to FeS-dominated surface chemistry. The dataset is balanced across the three regimes and the three steels.

3.6. Predictive Models

Measured rates were compared against three forms of the de Waard-Milliams family of semi-empirical CO₂ corrosion models: the 1991 baseline (scale-free) model, which depends on temperature and CO₂ partial pressure; a scale-corrected form that applies the FeCO₃ scaling-temperature factor; and a flow-coupled form in which the reaction-controlled rate is combined in series with a velocity- and diameter-dependent mass-transfer rate. The NORSOK M-506 framework is used as a reference point for the role of wall shear stress and the temperature-dependent pH function; its trends are discussed alongside the de Waard-Milliams results. These semi-empirical and analytical corrosion-rate modelling approaches follow established published forms [4] [5]. The benchmark was performed on the subset of uninhibited, general-corrosion records, because the models predict uninhibited base rates.

3.7. Statistical Analysis

Distributions of corrosion rate were summarized by regime and grade. Pearson correlation coefficients quantified the dependence of corrosion rate on the operating drivers. Model performance was assessed using the ratio of measured to predicted rate, reported as the median ratio and the percentage of points falling within a factor of two of the prediction, both overall and by service regime. The statistical significance of each correlation was assessed with a two-tailed test at the 0.05 level, and 95% confidence intervals (CI) were obtained from the Fisher z-transformation; correlations that were weak and not statistically significant are not interpreted as meaningful dependencies.

4. Results

4.1. Dataset Overview

Table 1 summarizes the operating envelope of the dataset. Temperature spanned 37 - 134 degC, total pressure 13 - 121 bar, CO₂ partial pressure 0.67 - 19.76 bar, H₂S partial pressure 0.00 - 1.23 bar and chloride 14,700 - 238,400 mg/L, covering conditions from mildly corrosive condensed water to highly saline sour brine. **Table 2** shows the balanced design, with 90 records distributed evenly across three steels and three service regimes.

4.2. Corrosion Rate by Service Regime and Grade

Measured corrosion rates ranged from 0.12 to 14.97 mm/yr, with a mean of 2.29 mm/yr and a median of 1.39 mm/yr. **Figure 1** shows the distribution by service regime. Median and upper-range rates increased from sweet to mixed to sour service, consistent with the higher measured rates observed where H₂S is present. The

spread within each regime was wide, reflecting the influence of temperature, pH, chloride, flow and inhibitor availability that is examined next.

Table 1. Summary of the field dataset operating envelope (N = 90).

Variable	Minimum	Mean	Maximum
Corrosion rate (mm/yr)	0.12	2.29	14.97
Temperature (degC)	36.90	86.39	134.00
Total pressure (bar a)	12.70	55.69	121.30
pCO ₂ (bar)	0.67	6.86	19.76
pH ₂ S (bar)	0.00	0.25	1.23
<i>In-situ</i> pH	4.09	5.29	6.36
Chloride (mg/L)	14,700	114,614	238,400
Flow velocity (m/s)	0.39	3.07	7.38

Table 2. Number of records by steel grade and service regime.

Steel grade	Sweet	Mixed	Sour	Total
API 5L X52 PSL2	10	10	10	30
API 5L X65 PSL2	10	10	10	30
ASTM A106 Grade B	10	10	10	30
Total	30	30	30	90

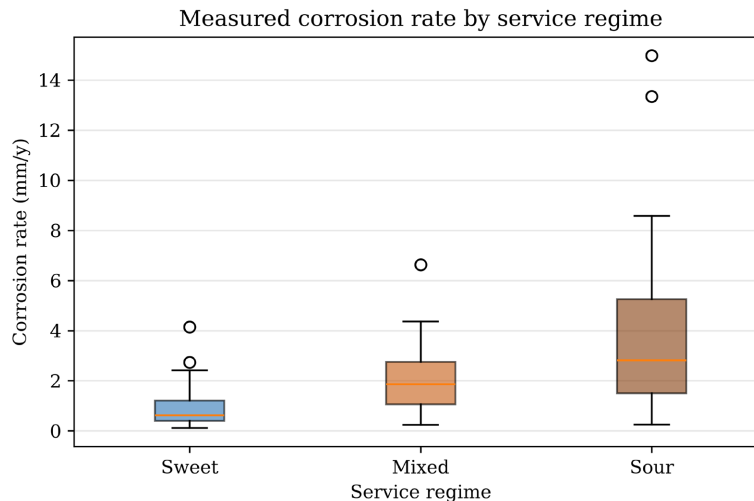


Figure 1. Measured field corrosion rate by service regime (sweet, mixed, sour).

4.3. Dependence on Operating Drivers

Figure 2 plots corrosion rate against the principal drivers. Across the full dataset (n = 90), corrosion rate was most strongly and significantly correlated with *in-situ* pH ($r = -0.49$; 95% CI $[-0.63, -0.32]$; $p < 0.001$) and H₂S partial pressure ($r = +0.42$; 95% CI $[+0.24, +0.58]$; $p < 0.001$), and significantly with temperature ($r = +0.30$; $p = 0.004$) and flow velocity ($r = +0.29$; $p = 0.005$). By contrast, the corre-

lations with CO_2 partial pressure ($r = +0.16$; 95% CI $[-0.05, +0.36]$; $p = 0.13$) and chloride ($r = +0.17$; 95% CI $[-0.04, +0.36]$; $p = 0.12$) were weak and not statistically significant at the 0.05 level, and are therefore not interpreted as meaningful dependencies. The strong inverse dependence on pH and the positive dependence on H_2S partial pressure are consistent with established $\text{CO}_2/\text{H}_2\text{S}$ corrosion mechanisms, in which acidification and sulfide surface chemistry promote metal dissolution.



Figure 2. Measured corrosion rate versus operating drivers, coloured by service regime.

4.4. The Sweet-to-Sour Regime Map

Figure 3 maps every record in the $p\text{CO}_2$ - $p\text{H}_2\text{S}$ plane, with corrosion rate shown on a colour scale and the $p\text{CO}_2/p\text{H}_2\text{S} = 500$ and 20 boundaries marked. The dataset populates all three regimes and a broad range of partial pressures, providing the coverage required to test predictive models from sweet through sour conditions. The highest rates concentrate toward the lower-right of the map, where H_2S partial pressure is appreciable relative to CO_2 .

4.5. Benchmark against Predictive Models

The 27 uninhibited, general-corrosion records were compared against the three model forms (**Figure 4**, **Table 3**). The de Waard-Milliams 1991 baseline systematically over-predicted measured field rates, by more than an order of magnitude on average (median measured/predicted ratio 0.05), with no points falling within a factor of two of the prediction. Applying the FeCO_3 scaling-temperature correction improved the agreement substantially (median ratio 0.18; 11% of points

within a factor of two), and the flow-coupled form gave an intermediate result (median ratio 0.11). Even with the scale correction, the models continued to over-predict for most records, indicating that protective scaling and the presence of H₂S reduce real field rates well below the CO₂-only worst case.

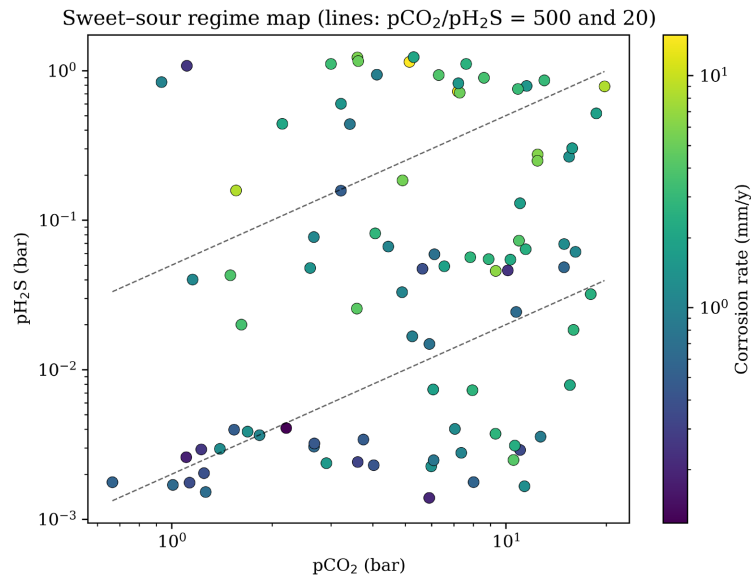


Figure 3. Sweet-to-sour regime map in the pCO₂-pH₂S plane; dashed lines mark pCO₂/pH₂S = 500 and 20.

Table 3. Mean measured rate and mean measured/predicted ratio by regime (uninhibited general-corrosion records, n = 27). CR in mm/yr.

Regime	n	Measured	dWM-1991 pred	dWM-1991 ratio	dWM-scale pred	dWM-scale ratio	dWM-flow ratio
Sweet	9	0.82	22.0	0.07	10.0	0.10	0.14
Mixed	9	2.27	51.4	0.07	10.3	0.23	0.10
Sour	9	3.99	72.5	0.09	10.3	0.43	0.16

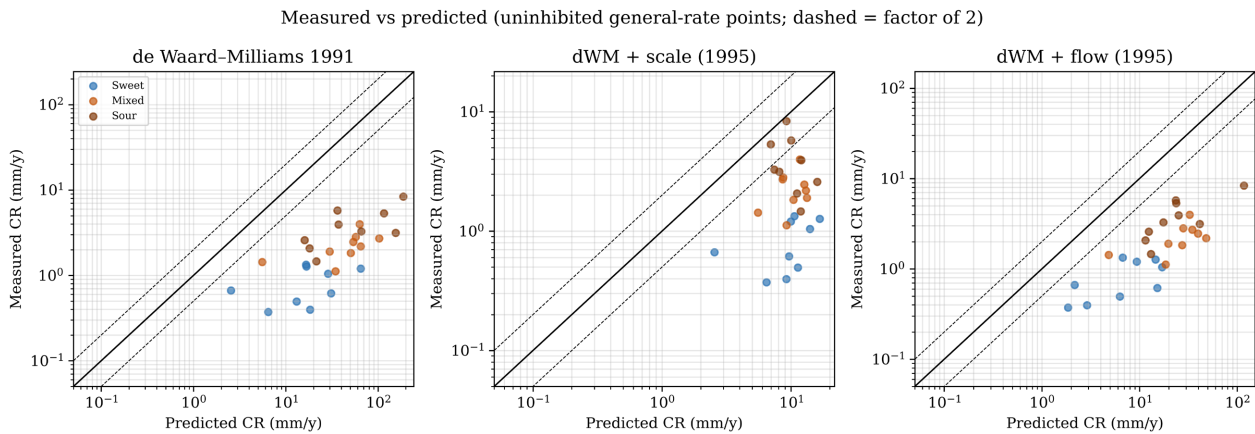


Figure 4. Measured versus predicted corrosion rate for the three model forms; solid line is parity, dashed lines mark a factor of two.

4.6. Regime Dependence and the H₂S Effect

The deviation between measured and predicted rates depended systematically on service regime. For the scale-corrected model, the mean measured/predicted ratio rose from 0.10 in sweet service to 0.23 in mixed service and 0.43 in sour service (**Table 3**), *i.e.* the CO₂-only model was most conservative in sweet conditions and least conservative as H₂S became significant, where measured rates approached the predicted values. **Figure 5** shows the measured/predicted ratio as a function of H₂S partial pressure, confirming that the discrepancy narrows as sour conditions are approached. Because the models contain no H₂S term, this trend reflects the genuine contribution of sulfide chemistry to the field rates rather than any model input.

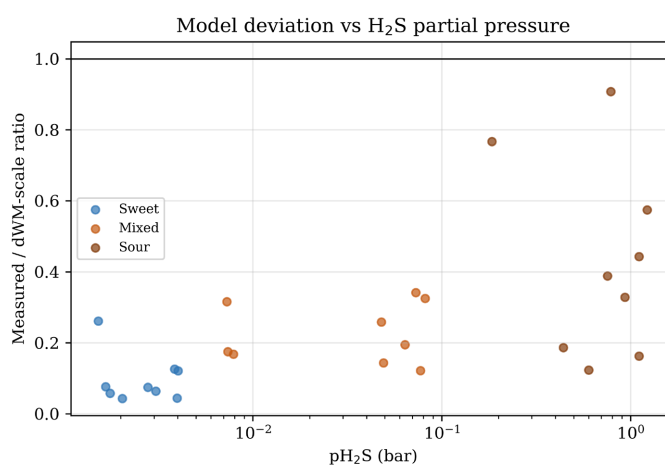


Figure 5. Measured/predicted (scale-corrected) ratio versus H₂S partial pressure, by regime.

4.7. Effect of Inhibition

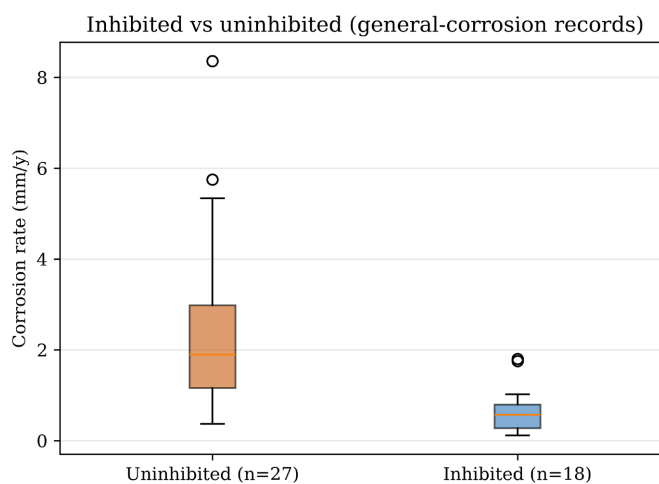


Figure 6. Corrosion rate for uninhibited versus inhibited records (general-corrosion records only).

Restricting the comparison to general-corrosion records, consistent with the rate-basis distinction defined in Section 3.3 and avoiding any pooling of general and localized rates, inhibited records corroded at a mean of 0.65 mm/yr ($n = 18$) versus 2.36 mm/yr ($n = 27$) for uninhibited records, a reduction of approximately 73% (Figure 6). This confirms the expected effectiveness of the applied chemical programs and justifies restricting the model benchmark to uninhibited records, since the predictive models estimate uninhibited base rates.

5. Discussion

The central result is that CO₂-only engineering models, applied in their uncorrected form, are strongly conservative against real field rates for these steels and services. The de Waard-Milliams 1991 baseline over-predicted by more than an order of magnitude, which is consistent with its design intent as a scale-free worst case and with the well-known observation that protective FeCO₃ scaling lowers real rates at field temperatures. Introducing the scaling-temperature correction moved predictions much closer to the data, in line with the dual role of temperature, which accelerates kinetics but promotes protective scale formation as it rises [11]. The flow-coupled form produced intermediate predictions, reflecting the additional influence of mass transfer that the shear-stress treatment in NORSOK M-506 also seeks to capture [12].

The regime dependence of the deviation is the most informative finding. Because none of the de Waard-Milliams forms includes an H₂S term, the systematic narrowing of the measured/predicted gap from sweet to sour service must originate in the data: H₂S raises field corrosion rates toward, and in some records beyond, the CO₂-only predictions. This is consistent with laboratory evidence that iron sulfides dominate the corrosion product and damage morphology of line-pipe steels at appreciable H₂S contents [3], and with mechanistic findings that steel metallurgy and surface films control localized attack [6]; it cautions against applying sweet models, even scale-corrected, to mixed or sour service without an explicit sulfide treatment. The significant inverse correlation of rate with *in-situ* pH and the significant positive correlation with H₂S partial pressure reinforce a mechanistic interpretation centred on acidification and sulfide surface chemistry; by contrast, the weak and statistically non-significant correlations with CO₂ partial pressure and chloride indicate that, within this dataset, neither acts as an independent first-order control on the measured rate.

These observations have practical implications for integrity management and prediction. First, corrosion-rate predictions used for inspection planning and remaining-life estimation should incorporate scaling corrections and an explicit H₂S treatment in mixed and sour service; relying on uncorrected sweet models will substantially overstate rates and may misallocate inspection effort. Second, the wide within-regime scatter shows that partial pressures alone do not determine the rate, water chemistry, flow and especially inhibitor availability are decisive, consistent with field experience that inhibitor programs and produced-water

management strongly govern outcomes [1] [7] [14]. The large rate reduction achieved by inhibition in this dataset, and the body of work demonstrating high inhibition efficiencies for oilfield and pipeline steels using both engineered and biomass-derived inhibitors [15]-[18], underline that environmental control is the primary lever once a susceptible carbon steel is in service.

The same CO₂/H₂S environments that drive the wall-loss rates quantified here also elevate the risk of environmentally assisted cracking, including sulfide stress cracking and stress-corrosion cracking, which have been documented in line-pipe case studies and failure analyses [9] [10] and which sit alongside alkaline cracking mechanisms treated elsewhere [19]. Cracking susceptibility was outside the scope of the present rate-focused dataset, but the operating windows mapped here identify the high-H₂S, low-pH conditions where cracking assessment should accompany wall-loss prediction. The study has limitations. The dataset, although balanced and broad, derives from a finite set of assets and monitoring campaigns; the records are period-averaged rather than continuous; localized-corrosion records are fewer than general-corrosion records; and the NORSOK M-506 model was used as a reference framework rather than computed point-by-point. Extending the dataset across additional operators and incorporating an explicit, validated H₂S corrosion model are clear directions for further work.

6. Conclusions

A field dataset of 90 corrosion-rate measurements for three common oilfield steels (API 5L X52, API 5L X65 and ASTM A106 Grade B), each paired with quantified operating drivers and spanning sweet, mixed and sour service, was assembled and analysed.

Measured rates ranged from 0.12 to 14.97 mm/yr and increased significantly with H₂S partial pressure ($r = +0.42$, $p < 0.001$) and with decreasing *in-situ* pH ($r = -0.49$, $p < 0.001$), whereas the correlations with CO₂ partial pressure ($r = +0.16$, $p = 0.13$) and chloride ($r = +0.17$, $p = 0.12$) were weak and not statistically significant.

The uncorrected de Waard-Milliams 1991 model over-predicted field rates by more than an order of magnitude (median measured/predicted ratio 0.05); the FeCO₃ scaling correction improved agreement (median ratio 0.18; 11% within a factor of two) but still over-predicted most records.

The measured/predicted deviation depended systematically on service regime, narrowing from sweet to sour service, which, because the models contain no H₂S term, demonstrates the genuine contribution of sulfide chemistry to field rates.

Among general-corrosion records, inhibited assets corroded approximately 73% slower than uninhibited assets, confirming that environmental control is the primary mitigation lever and supporting the use of explicit scaling and H₂S treatments when predicting rates for inspection planning in mixed and sour service.

Data Availability and Anonymization Statement

The field dataset analysed in this study was obtained from operating oil and gas assets of an anonymous client operator and is reported in anonymized form; operator, field and well identifiers have been removed and assets are referred to by coded labels. Corrosion rates and operating conditions are reported as measured. Aggregated data supporting the findings are available from the author on reasonable request, subject to the data-owner confidentiality agreements.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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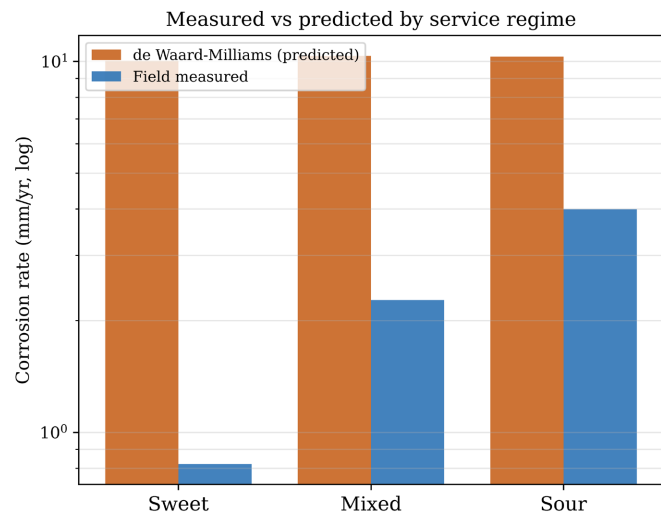
Graphical Abstract

Field CO₂/H₂S Corrosion of Oilfield Carbon & Low-Alloy Steels

90 field measurements - API 5L X52/X65, A106-B

across the sweet -> mixed -> sour spectrum

- Rates rise with H₂S ($r = +0.42$) and falling pH ($r = -0.49$)
- CO₂-only models over-predict field rates by ~14x
- Scale correction helps; gap narrows toward sour service
- H₂S contribution is real - sweet models miss it



Graphical abstract: field-measured corrosion rates versus de Waard-Milliams (scale-corrected) predictions across the sweet-to-sour spectrum, with the over-prediction factor shown for each regime.