CO$_2$ CORROSION MODEL VERIFICATION USING FIELD DATA

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ABSTRACT

An integrated multiphase flow and corrosion prediction package was tested by comparing it's performance with data obtained from the field. The comparisons indicated a satisfactory performance, even for the situations where incomplete information was available about the field cases. The results have shown that the effect of traces of H$_2$S on CO$_2$ corrosion needs to be given particular care when making simulations.

Keywords: field data, CO$_2$ corrosion, pipeline, H$_2$S, model, carbon steel

INTRODUCTION

In CO$_2$ corrosion, various factors related to metallurgy, chemical/electrochemical kinetics and hydrodynamics affect the corrosion rate. An overview that focuses on the impact of steel composition and surface films has been given recently by Kermani[1], other factors were discussed by Nesic in 2003.[2] In the latter case, various strategies in modeling CO$_2$ corrosion were discussed ranging from truly mechanistic to purely empirical. More than a dozen corrosion prediction models have been developed during last few decades. From the early de-Ward model [3,4] to most recent Nešić's model [2, 5-9], progressively more factors have been considered and incorporated into the calculations, in some cases by introducing correction factors or empirical correlations, in others by incorporating truly mechanistic expressions into the models.

A different overview of CO_2 corrosion prediction models and their predictability had been given Nyborg in 2002[10]. Some limited comparisons with field data were done and a range of models was evaluated. A similar exercise was done in the present project, except that only one model was used: the Ohio University's integrated multiphase flow and corrosion prediction package MULTICORP V3.0 (in further text below referred to as the "*Model*").

Before the *Model* is briefly outlined below and comparisons made, a few remarks are in place. It is common knowledge that models are "representations of reality" and in the best case are only as good as our understanding about that "reality" is. In practical words, the quality of the corrosion models is inseparable form the theory backing them, expressed in terms of equations and communicated to us by user-interfaces. However, no model, theoretical or empirical, can be trusted without an experimental verification. This "reality check" comes usually in the form of data collected typically in a laboratory setting and in some cases from the "real world" i.e. the field.

While empirical verification of corrosion models is a must, one important aspect of this process gets overlooked frequently. Empirical data can be erroneous, actually errors are always part of any empirical data, and it is not an issue of "if there are errors", the question to be asked is "how big are the errors". Errors are part of the process of collecting empirical data. Even laboratory data are riddled by errors which are often not reported or evaluated, even if this is not so difficult to do. The process of collecting data from the field is enormously more complicated and expensive than collecting lab data. For a variety of reasons that are difficult to control, field data are plagued with errors, coming from a variety of sources: uncontrolled process variations, inability to influence the process, failure of measurement/monitoring systems, transmission errors, human errors, etc. Sometimes the errors are so large that they render the field data all but useless. This is not to say that verifying models by using field data is not a good idea, to the contrary, it is the ultimate test that needs to be done whenever possible. However, extreme caution must be exercised to ensure that the field data themselves are believable, and that the degree of error associated with the field data is known.

If an experienced corrosion engineer cannot make sense of the field data, chances are slim that a corrosion model will. Therefore asking of any model to "predict" empirical data, which we ourselves cannot explain, is a bound to be a futile exercise. In some exceptional cases the models are able to capture the complexity which may initially defy our own ability to grasp it, but in the end the models are only as good as the knowledge built into them. Good models can be of great assistance to a corrosion engineer but they cannot perform miracles.

The *Model* evaluated in the present study was extensively calibrated and verified with a large set of verified laboratory corrosion data and this has been reported previously.[6,8] In the text below some comparisons between the simulations made with the *Model* and selected field data are shown.

FEATURES OF THE MODEL

The background details about the transient mechanistic CO_2 corrosion prediction *Model*, have been published previously[5,6,8,11,12]. In this section only a outline of the *Model*'s capabilities features is given to facilitate following of main arguments in the subsequent text. The *Model* covers almost all key aspects of internal corrosion of mild steel oil and gas pipelines and is based on solid theoretical foundations, which include the models of:
  - Kinetics of electrochemical reactions at the steel surface;

- Dynamics of coupled transient transport of multiple species between the bulk solution and the steel surface, through the turbulent boundary layer and through a porous surface film;
- Kinetics of chemical reactions including precipitation;
- Growth of iron carbonate films.

Therefore it is possible to reliably predict the effects of key variables that affect internal pipeline corrosion such as:

- Effect of multiphase flow
- Effect of temperature
- Effect of CO_2 partial pressure
- Effect of pH and brine chemistry
- Effect of H_2S and organic acids
- Effect of steel type
- Effect of inhibition by crude oil and/or corrosion inhibitors
- Magnitude and morphology of localized attack

As the *Model* is based on a mechanistic (theoretical) model, the equations behind it are faithful descriptors of the important physico-chemical processes underlying corrosion. This is in contrast with the other models, most of which are empirical or semi-empirical. This mechanistic approach offers many advantages some of which are listed below:

- Besides providing immediate answers – e.g. the corrosion rate, the *Model* allows the users to get a deeper insight into the root causes behind the problem, thereby raising the user's confidence in the provided answer. The empirical models based on arbitrary mathematical equations lack this capability, completely or in part.
- Due to the strong theoretical background, the user can extrapolate the predictions made by the *Model* outside the calibration domain with much more confidence then can ever be achieved with the (semi) empirical models whose extrapolation capabilities are questionable.
- Any extensions of the *Model* to include new phenomena (for example the effects of high H_2S concentrations, sand, etc.) can be done relatively easily, in a logical fashion, and without changing most of the existing coding. This is in contrast with the extensions of (semi) empirical models which are cumbersome and often prohibitively difficult.

The *Model* seamlessly integrates a *corrosion model* with a *multiphase flow model* a feature much needed by the corrosion engineers. It enables successful prediction of one of the most important multiphase flow effects on corrosion which is related to water wetting and entrainment of water by the oil phase. The *Model* enables fundamentally correct and reliable prediction of conditions where protective iron carbonate films form which can help mild steel survive the corrosive conditions found in pipelines. Other models are either incapable of predicting protective film formation or have arbitrary and dubious factors to account for this phenomena. The *Model* has a full blown model of the effect of organic acids built in. The same is true for a unique model of corrosion inhibition by crude oils.

FIELD CASE SIMULATION

Case #1: Oil Pipeline

The pipeline simulated in case #1 is an approximately 6 km long pipe section from a total 24 km long offshore pipeline, 24″ ID, carrying oil (and water). Pipeline topography shows that there are only slight changes in inclination (see Table 1). For simulation, the section is divided into 10 subsections based on the topography information. As seen in Table 1 the pressure and temperature at the inlet of the simulated section are approximately 24 bar and 44 ^{o}C respectively and decrease to 22 bar and 39°C at the outlet. After the separation on the platform it is found that the mixture contains typically a 1% water cut. Based on the pipe ID, this translates to below 0.01m/s superficial water velocity what is the suggested lower limit in the software based on calibration data which did not include such low water flow rate situations. Therefore the hydrodynamic *Model* is extrapolating in this case. Bearing in mind that the *Model* resides on strong theoretical background, the extrapolation is not considered a problem.

CO_2 content in the gas phase inside this pipeline is about 3 mol%. The content of H_2S is reported to be 15 ppm in the gas phase. Field experience shows that the amount of H_2S can decreases gradually along the pipeline due to continuously consumption by formation of a FeS film on the steel surface. Therefore, based on the suggestion by the operating company, it has been assumed in the simulation that by the time the fluids entered this section of the line, H_2S content was reduced to 0.5 ppm, and kept decreasing. The validity of the assumption will be discussed later.

Since the pressure and temperature profiles along the pipeline were not available, it was assumed in the simulation that temperature linearly decreases from the inlet to the outlet mainly due to the dissipation of heat into the ambient environment. Overall pressure drop (which is in general a result of friction, kinetic energy loss, and elevation changes) is also assumed to be linear along the pipeline. As the changes of pressure and temperature from inlet to outlet are quiet small, these assumptions should be reasonably accurate.

The total measured organic Ac$^-$ content and HCO_3^- concentration are 310 and 672 mg/L, respectively. Given the water chemistry, the software was used to calculate the pH which was in a range from pH5.8 to pH6. The measured Fe^{2+} content is relatively low (3.3 mg/L). Consequently, the calculations suggest that no significant amount of $FeCO_3$ film would form on the internal pipe wall particularly at the relatively low temperatures of 40°C.

FIGURE 1 shows the comparison of predicted corrosion rates with field corrosion rates which were measured by the intelligent pigging method. Maximum and time-averaged field corrosion rates were selected from each sub-section for comparison. Generally, the current *Model* predicts the trend correctly and is generally conservative, as the corrosion rates are typically close to the maximum measured corrosion rates. When making judgments about the comparison with any model, one has always to consider the accuracy of the field data. For example, in this case the uncertainty associated with H_2S concentration affects the simulation greatly. A sensitivity study of H_2S concentration effect shows that by assuming a higher H_2S concentration (e.g. a few ppm) would result in a lower prediction for the corrosion rate which would be very close to the averaged field values. Assuming the full 15 ppm H_2S, the predicted corrosion rates would be reduced to approximately 0.4 mm/y what falls below the lower bound of the field data.

Case #2: Oil-Gas pipeline

Detailed operating conditions are listed in Table 2 for a 10″ ID, 6.3 km long oil-gas (and water) multiphase pipeline with three tie-ins. The pipeline thus consists of 4 sections with different oil and gas flow rates and water cuts. Topography of this pipeline indicates a wide inclination range from -7.6 degrees (downward flow) to 11.5 degrees (upward flow). It is then expected that different kinds of flow patterns would be encountered due to many changes in pipeline inclination. Recorded temperatures at inlet and outlet are 65 to 58 $^{\circ}$C, respectively with the pressures being 28 bar and 8 bar respectively. Again, a linear drop for pressure and temperature along the pipe was assumed to simplify the calculation. This assumption might initially not sound very plausible in this case as pressure drop varies unevenly due to the change in flow patterns and inclinations. However, a sensitivity study carried out showed that the rate determining process is not the flow or the temperature profile, and therefore the simple linear assumption holds.

H_2S in the gas phase is reported as less than 10 ppm and no assumptions have been made to account for the consumption of H_2S for this pipeline based on the fact that there are three tie-ins to the pipeline, which are assumed to roughly maintain the same composition in gas phase. The CO_2 content is 0.5 mol% and the total Ac^- content and HCO_3^- concentration are 100 and 49 mg/L, respectively. Fe^{2+} content in the water is fairly low (<0.1 ppm) and pH is approximately 6.0 so that the formation of $FeCO_3$ film is not feasible due to a low supersaturation.

FIGURE 2 shows a comparison of the corrosion rates from the simulation and the field measurements along the pipeline. It is seen that the field corrosion rate data are very scattered, ranging from 0 to 0.9 mm/yr. Actually the scatter is so large that questions must be raised about the reasons for this variation and the validity of such field data. However, this issue is outside the scope of the present paper. In general, the corrosion rates predicted by the *Model* fall into the scatter range of the field data. In the first 4 km, the predicted corrosion rates are at the upper bound of the field measured corrosion rates, while predicted corrosion rates are close to the lower bound of the field data for the last 2 km pipeline. The predicted decrease is mainly a result from the drop of CO_2 partial pressure which is related to a decrease in system pressure along the pipeline. The sensitivity study again indicated the importance of the trace amounts of H_2S content in the system, which affected the predicted corrosion rates greatly. The results of the sensitivity study might be used as a starting point when considering the large scatter seen in the field data.

Case #3: Oil-Gas Well

As shown in Table 3, this 6″ ID multiphase well features high pressure (116 – 276 bar) and temperature (91 – 116 $^{\circ}$C), some of which are not within the suggested maximum limits by current version of the software. This is a near vertical line with an inclination of approximately 85 degrees so that it is feasible to use a linear assumption for pressure drop since most of the pressure loss will result from the hydrostatic effect. Temperature profile is again simplified as linear from bottom to wellhead.

The CO_2 content in the gas phase of this multiphase line is about 3 mol% and the total Ac^- and HCO_3^- concentrations are 28 and 331 mg/L, respectively. Only 2.5 ppm H_2S in the gas phase is reported and the Fe^{2+} content is low (0.18 ppm) and no $FeCO_3$ precipitation is predicted. The field reports indicates high corrosion rates in the range from 1 to 5 mm/yr which were confirmed by a leakage (the exact location of leakage is not known). However, the predicted corrosion rates are much higher than 5 mm/yr (as shown in FIGURE), especially at the bottom sections of the well. At

the given conditions, it is obvious that a high corrosion rate is expected at the calculated pH5.2 and high temperature in the absence of protective $FeCO_3$ formation.

Cases #4: without H_2S

Cases #1-3 have demonstrated that small amounts of H_2S (traces) can have a significant effect on the CO_2 corrosion rate. It is thus very interesting to carry out some simulations with field cases without H_2S. Table 4 lists a series of simulations for the systems where "sweet" i.e. CO_2 corrosion prevails.

Case (4a) shows the corrosion rate prediction of a 12 inch oil well under various operating conditions. Simulated temperature range varies from 57 to 104 ^{o}C and the water production rates are 40 or 671 m^3/day. It can be seen that the predicted corrosion rates fall exactly into the field data range which was reported as 4.6 to 10 mm/yr. Furthermore, since pH, inclination, and CO_2 partial pressure vary only slightly, the temperature is the most influential factor in this system.

In case (4b) when compared to the field data, *Model* predicts an approximately 2 times higher corrosion rate for this multiphase flow pipeline. Pure water ("natural") pH (~4.0) is calculated from the CO_2 partial pressure as there was a lack of detailed water chemistry data, that might have contributed to the discrepancy between the predictions and field data.

In case (4c), HCO_3^- and HAc contents vary slightly in the solution while other parameters remaining almost the same. Predicted corrosion rates change from 2.6 mm/yr at the condition of 49 ppm HCO3$^-$ and 100 ppm HAc to 0.46 mm/yr at the condition of 100 ppm HCO_3^- and 0 ppm HAc. It is clear that the average corrosion rate is close to the field measured corrosion rate which is about 1.1 mm/yr.

CONCLUSIONS

- The capability of *Model* to predict the corrosion rate under various field conditions has been demonstrated by comparison with field data.

- The results have shown that the effect of traces of H_2S on CO_2 corrosion needs to be given particular care when making simulations.

- Overall, the simulation results indicated a satisfactory performance of the *Model*. The purpose of this exercise was not to match field data "exactly" by changing *Model* parameters or arbitrarily choosing *Model* inputs rather than to check the performance of the *Model* and identify the key parameters for cases when only limited field information is available.

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TABLE 1

CASE #1: OPERATION CONDITIONS FOR A 24‴" OIL/WATER PIPELINE

Pipe Section	θ	T	D_{in}	V_{so}	V_{sw}	P_{total}	P_{CO2}	P_{H2S}
#	degree	°C	m	m/s	m/s	bar	mol%	ppm
1	0	44.0	0.581	0.59	0.006	24.0	3	0.5
2	1	44.0	0.581	0.59	0.006	24.0	3	0.5
3	-2	44.0	0.581	0.59	0.006	24.0	3	0.4
4	1	44.0	0.581	0.59	0.006	24.0	3	0.4
5	-1	43.9	0.581	0.59	0.006	24.0	3	0.3
6	0	43.9	0.581	0.59	0.006	24.0	3	0.3
7	0	43.8	0.581	0.59	0.006	23.9	3	0.0
8	0	43.6	0.581	0.59	0.006	23.9	3	0
9	0	43.2	0.581	0.59	0.006	23.8	3	0
10	0	39.1	0.581	0.59	0.006	22.2	3	0

Notes:

θ Inclination (negative: downward flow; positive: upward flow)

T   Temperature

D_{in} Inner diameter of the pipeline

V_{so} Superficial velocity of oil phase

V_{sw} Superficial velocity of water phase

P_{total} Total pressure

P_{CO2} CO2 content in the gas phase

P_{H2S} H2S content in the gas phase

TABLE 2

CASE #2: OPERATION CONDITIONS FOR A 10″ OIL/WATER/GAS PIPELINE

Pipe Section	θ	T	P_{total}	P_{CO2}	V_{opr}	V_{wpr}	V_{gpr}	pH	V_f	Flow Pattern
#	degree	°C	bar	bar	m^3/d	m^3/d	MSm^3/d		m/s	
1		65.0	28.0	0.140	160.0	112.0	0.056	5.60	0.13	ST
2	0.0	64.6	27.0	0.135	400.0	248.0	0.14	5.70	0.32	ST
3	11.5	64.5	26.6	0.133	400.0	248.0	0.14	5.70	3.83	ST
4	8.3	63.4	23.5	0.118	400.0	248.0	0.14	5.70	0.33	SLUG
5	6.9	63.4	23.3	0.117	400.0	248.0	0.14	5.70	0.34	SLUG
6	-0.5	63.3	23.0	0.115	400.0	248.0	0.14	5.70	4.68	ST
7	0.0	63.2	22.8	0.114	2780.0	834.0	0.973	5.70	0.34	ST
8	0.0	62.8	21.8	0.109	2780.0	834.0	0.973	5.74	1.95	SLUG
9	-2.7	62.5	20.7	0.104	2780.0	834.0	0.973	5.80	3.08	SLUG
10	-3.5	61.3	17.4	0.087	2780.0	834.0	0.973	5.80	1.43	SLUG
11	0.0	60.6	15.5	0.078	4450.0	1335.0	1.5575	5.90	3.48	SLUG
12	-7.6	60.6	15.5	0.077	4450.0	1335.0	1.5575	5.90	12.86	SLUG
13	6.7	60.5	15.1	0.076	4450.0	1335.0	1.5575	5.90	6.61	SLUG
14	1.1	59.8	13.2	0.066	4450.0	1335.0	1.5575	5.90	0.92	ANNU
15	1.4	58.9	10.7	0.053	4450.0	1335.0	1.5575	6.00	1.01	ANNU
16	0.0	58.2	8.7	0.043	4450.0	1335.0	1.5575	6.10	4.36	SLUG

Notes:

V_{opr}	Oil production rate
V_{wpr}	Water production rate
V_{gpr}	Gas production rate
V_f	In-situ water film velocity
ST	Stratified flow
ANNU	Annular flow

TABLE 3

CASE #3: OPERATING CONDITIONS FOR A 6″ OIL-WATER-GAS WELL

distance	θ	T	P_{total}	P_{CO2}	V_{opr}	V_{wpr}	V_{gpr}	D_{in}	pH	V_f	Flow Pattern
m	degree	°C	bar	bar	bbl/day	bbl/day	MSm^3/d	m		m/s	
0	85.0	116.0	276.4	8.292	10500.0	3011.0	42.5	0.16	5.2	3.63	Slug
1428	85.0	109.0	231.4	6.941	10500.0	3011.0	42.5	0.16	5.2	3.90	Slug
2285	85.0	104.3	201.4	6.041	10500.0	3011.0	42.5	0.16	5.2	4.16	Slug
3142	85.0	99.6	171.3	5.140	10500.0	3011.0	42.5	0.16	5.2	4.50	Slug
3999	85.0	94.9	141.3	4.239	10500.0	3011.0	42.5	0.16	5.2	4.90	Slug
4570	85.0	91.0	116.3	3.489	10500.0	3011.0	42.5	0.16	5.2	5.37	Slug

Notes: H_2S content is 2.5 ppm, pH is calculated based on the given water chemistry

TABLE 4

## CASE 4: CORROSION RATE PREDICTION FOR CASES WITHOUT H_2S

Cases	T	P_{total}	P_{CO2}	V_{opr}	V_{wpr}	V_{gpr}	D_{in}	θ	Predicted pH	Predicted CR
#	°C	bar	bar	m^3/d	m^3/d	m^3/d	m	degree		mm/yr
4a	57	270	1.56	760	40	-	0.1	88	5.05	4.4
	80	250	1.56	549	671	-	0.1	88	--	6.9
	66	287	1.56	760	40	-	0.1	84	4.92	5.3
	85	269	1.56	549	671	-	0.1	84	5.1	7.5
	107	369	1.56	549	671	-	0.1	84	5.06	10.9
	104	375	1.56	760	40	-	0.1	88	5.06	10.3
4b	54	95	1.2	450	50	5x10^6	0.308	0	4.0	10.0
4c	58.7	12.9	0.0645	4450	1907	1.56x10^6	0.258	0	5.74	2.6
	58.7	12.9	0.0645	4450	1907	1.56x10^6	0.258	0	6.3	0.5

Notes:

Case 4a: Field reported corrosion rates are 4.6 to 10.0 mm/yr

Case 4b: Field reported corrosion rates are ~4 mm/yr

Case 4c: Field reported corrosion rates are ~1.1 mm/yr
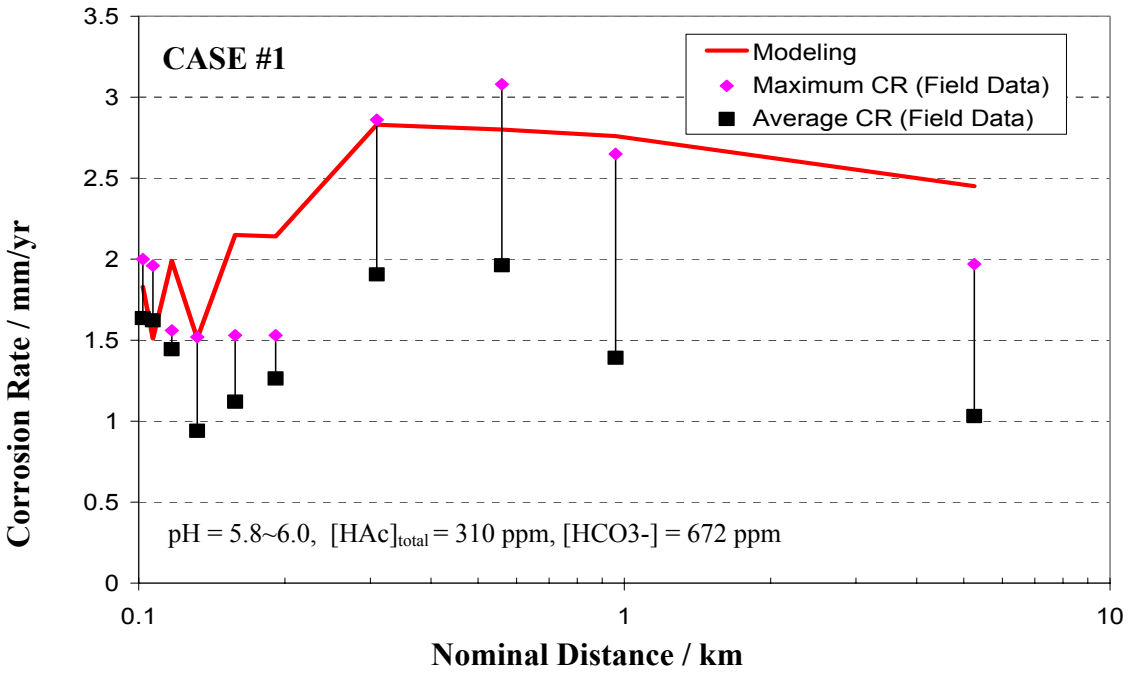
FIGURE 1. Comparison Of Predicted Corrosion Rate And Field Data (Case #1: 24″Oil)

Notes: the corrosion rate values are given for the center point of each simulated pipeline subsection; the origin of x-coordinate is arbitrary and not at pipeline inlet point; the maximum and minimum corrosion rates are determined from the field data within each sub-section only.
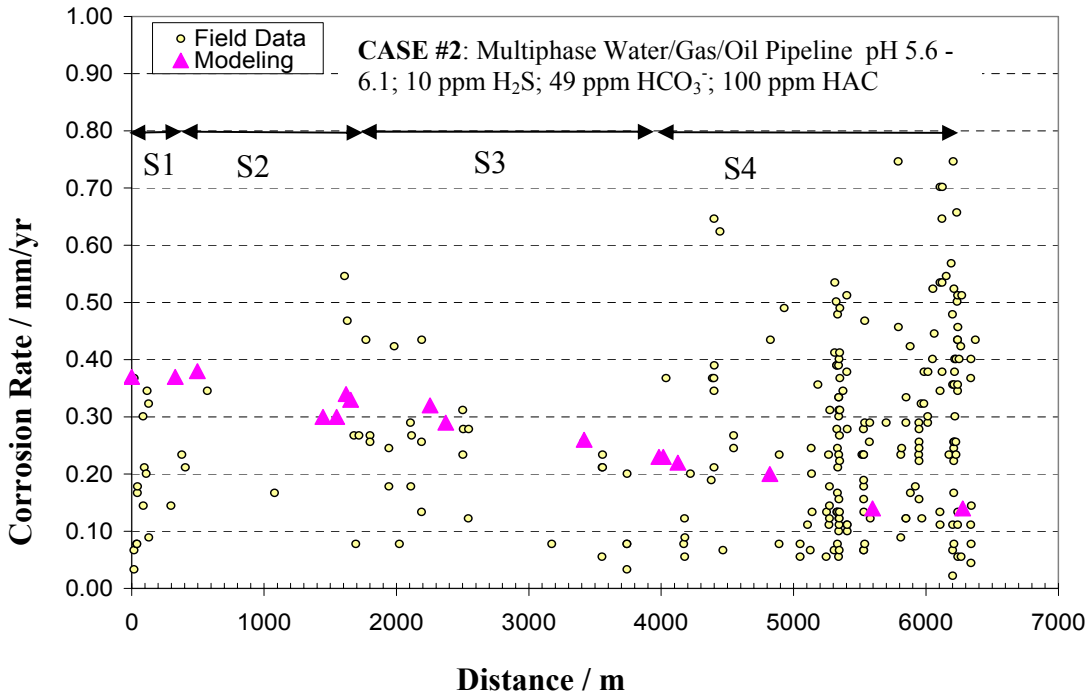
FIGURE 2. Corrosion Rate Simulation And Comparison Along The Pipeline

(S1, S2, S3, and S4 are pipeline sections with different oil/water/gas flow rates as listed in Table 2.)
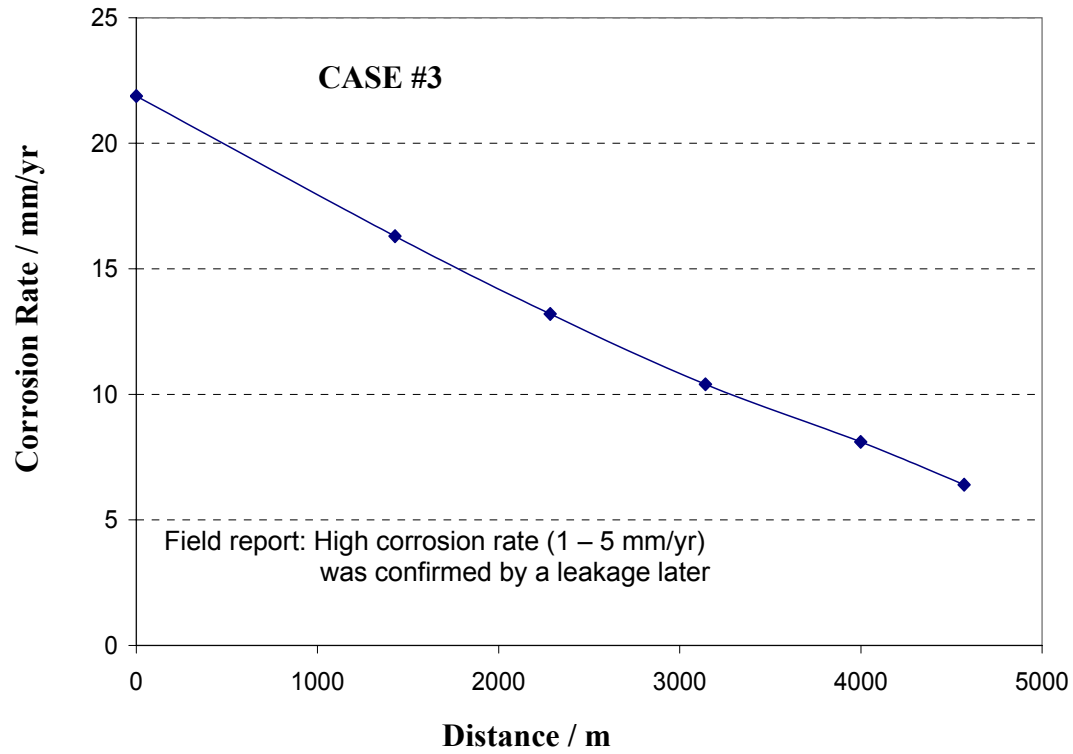
FIGURE 3. Corrosion Rate Simulation And Comparison Along The Pipeline (Case Three: Multiphase Well)