

NACE Publication 21413

Prediction of Internal Corrosion in Oilfield Systems from System Conditions

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Foreword

NACE technical committee reports are intended to convey technical information or state-of-the-art knowledge regarding corrosion. In many cases, they discuss specific applications of corrosion mitigation technology, whether considered successful or not. Statements used to convey this information are factual and are provided to the reader as input and guidance for consideration when applying this technology in the future. However, these statements are not intended to be recommendations for general application of this technology, and must not be construed as such.

The purpose of this technical committee report is to bring together state-of-the-art knowledge about corrosion prediction from system conditions, mostly for upstream oil and gas. The material presented is mostly based on observed industry practices for upstream oil and gas. However, the principles could be suitably applied in other petrochemical areas, such as midstream and downstream. Essentially, the discussion is based on second principles (applied) rather than first principles (fundamental).

The report intends to provide corrosion practitioners worldwide with a concise guide of the most important parameters impacting the prediction of corrosion rate like CO₂ and H₂S concentrations, presence of microbes, corrosion inhibitors, presence of hydrocarbons, nature of the steel (carbon steel or corrosion resistance alloys), presence of oxygen, and flow and erosion effects.

The prediction of corrosion rates from system conditions is usually done with the help of mathematical—and sometimes empirical—models. Attention is dedicated to existing prediction models, their limits of application, availability, as well as relevant specific references. An important effort was made to include all known models as well as their most relevant characteristics, limitations, availability, and range of application; however other models exist that were not brought to the attention of the technical committee.

In spite of the state-of-the-art knowledge and corrosion prediction models presented in this report, the gap between the predicted and actual corrosion rates is still significant. This is partially caused by the lack of precise definition of the actual environment, system conditions, and complex corrosion processes that are interacting with each other in the target application that is being simulated.

Scope

Section 1 provides the reader with an overview of critical parameters. Section 2 describes the main differences between the corrosion models considered in the report and provides a high level guideline to engage in corrosion prediction. Sections 3 to 11 provide details of each parameter considered.

Task Group (TG) 076 on Oil and Gas Production, Corrosion Prediction prepared this report in 2017. TG 076 is administered by Specific Technology Group (STG) 31 on Oil and Gas Production—Corrosion and Scale Inhibition, and is sponsored by STG 60 on Corrosion Mechanisms and STG 61 on Inhibition—Corrosion and Scaling. This report is issued by NACE International under the auspices of STG 31.

Introduction

This technical committee report brings together state-of-the-art knowledge about corrosion prediction from system conditions, mostly for upstream oil and gas. The material presented is mostly based on observed industry practices for upstream oil and gas. However, the principles could be suitably applied in other petrochemical areas, such as midstream and downstream. Essentially, the discussion is based on second principles (applied) rather than first principles (fundamental). It includes a comprehensive list of references, figures, and equations to create a concise guide of the most important parameters impacting the prediction of corrosion rate. This report is maintained by TG 076.

Keywords: CO₂, H₂S, MIC, oxygen corrosion, corrosion prediction models, oil and gas

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Section 1: Overall Corrosion Prediction

There are numerous models available to provide an assessment on the likely corrosiveness (aggressiveness) of oil field fluids. The majority is aimed at assessing the expected corrosion rates for carbon steel components, but some also cover expected performance of corrosion resistant alloys (CRAs) as well.

The various models considered (listed in Appendix A) cover the principal corrosion threats in oilfield fluids:

- Carbon dioxide (sweet) corrosion
- Hydrogen sulfide (sour) corrosion
- Microbiologically induced corrosion (MIC)
- Oxygen corrosion

They also consider the impact of variations as a result of flow, hydrocarbons, metallurgy and performance of corrosion inhibitors. Many of the sweet (CO_2) models are based on the original work by De Waard, Milliams, Lotz, and Dugstad.¹⁻³

Some sour corrosion models are developed primarily based on field data and field tests from Canadian sour gas and oil production pipelines.

The main differences between the different models relate to the extent to which they take into account the different factors that directly affect the general and pitting corrosion rate of carbon steel, such as formation of protective or semi-protective iron carbonate (FeCO_3) or iron sulfide (FeS) films, "oil wetting," flow effects, etc.⁴

The role of this report is to highlight some key issues to clarify the options available. NACE TG 447 is currently developing a report on steps to follow to select an appropriate model for a particular condition.

Section 2: Differences between Models

Because of the wide variety of CO_2 based models, most reviews normally use at least two and often three different models to provide improved confidence in any predictions.^{5,6} Where the results from different models for the same process simulation (i.e., combination of CO_2 partial pressure, operating temperature, flow rate, water cut, etc.) give predicted corrosion rates of similar value (typically within $\pm 20\%$) then it is normally considered that the predictions are consistent. However, where the predicted natural corrosion rates vary significantly (typically by more than $\pm 50\%$, or even more), then this is usually taken as indicative that the different assumption(s) used in the models is (are) significant with respect to the particular condition being considered.

A good example of this is the difference between the NO^(a) and CA models, in the temperature range 60 to 150 °C (140 to 302 °F), as shown in Figure 1 below. This shows the predicted corrosion rates for 8 mol% CO_2 , in a produced brine (200 mg/L bicarbonate and total ionic strength of 50 g/L), at an operating pressure of 500 kPa, with moderate flow (1 m/s). The NO model gives a peak corrosion rate (for carbon steel) of 9.5 mm/y at a temperature of approximately 60 °C (140 °F), which then drops away to a limiting value of 3.2 mm/y at 93 °C (200 °F) and drops down to 0.26 mm/y at 150 °C (302 °F) for temperatures greater than 130 °C (266 °F). The predicted corrosion from CA under the same conditions gives similar values up to about 70 °C (158 °F), but then does not show any reduction in corrosion rate with increase in temperature, giving a limiting value of approximately 14 mm/y (in the absence of any inhibitor).

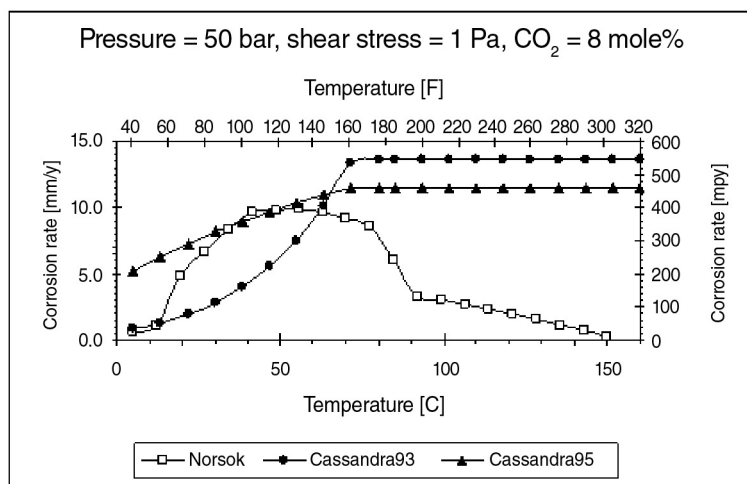


FIGURE 1: Comparison of Different Model Outputs for Same Input Parameters

The reason for this difference is the extent to which formation of a protective FeCO_3 scale is allowed for in the two models (while NO includes the formation of a protective scale, CA considers it to a limited extent). Similar variations are found between other models, especially where the effects of "oil wetting," presence of protective FeS film, or inhibitor performance with respect to flow rate are concerned.⁵

^(a)Refer to Appendix A for the model name acronyms used throughout this report.

Such variations do not mean that one model is wrong and the other right, just that in these circumstances the assumptions and degree that the model is considered to be conservative (that is, erring on the side of caution). The decision as to which prediction to use is in turn typically dependent on the person who is doing the assessment. Material selection reviews using the more optimistic (least conservative) model(s) (i.e., taking maximum contribution from oil wetting, scale formation, inhibitor performance, etc.) are used to “justify” selection of carbon steel; while others prefer a more cautious approach, taking the least contribution from these factors or even discounting them altogether, recognizing that they are likely identifying a worst case (and in some cases “non-credible”) condition.

A good example of this is the issue of oil wetting, where significant benefits (i.e., reduction in corrosion rate) are expected under normal operation conditions; however, many operators ignore this and expect the model to assume 100% water wet surface.

Variations in Conditions

It is commonly recognized that the operating conditions for a field/section of pipeline/item of equipment in a process plant are not the same everywhere or for all time. Hence, any assessment usually considers variations in location and in time. In some cases, any changes typically result in insignificant variations to the predicted corrosion rate (typically less than $\pm 10\%$); however, in other cases, this sometimes results in major variations of the corrosion rate ($\pm 100\%$ or more). This is often the case where the changes in conditions cross a threshold value. For example, the EC model assumes that once the linear velocity for a system exceeds the API⁽¹⁾ critical erosional velocity, all protective films become unstable and hence less effective. Small changes in the fluid conditions (such as flow rate, pressure, temperature, gas-oil ratio (GOR), etc.) could result in an increase of 2x to 5x in the predicted corrosion rate⁷. Hence, for system evaluation, the normal practice is to run the prediction models for different combinations of operating conditions.

Some models inherently take into account the variation of localized corrosion rates as a function of variation in operating parameters and have established boundaries. For example, the IF model inherently adjusts the localized corrosion rate based on field operating variations, based on established variation of the localized corrosion rate as a function of oil production rate, water production rate, gas production rate, solids, temperature, pressure, H₂S partial pressure, CO₂ partial pressure, and the effects of sulfate, bicarbonate, and chloride.

The effect of variations is typically accommodated by either running the selected model(s) with individual combinations of operating conditions, (for example on a year-by-year basis, based on changing predictions, as described in the NO model) or by plotting the predicted corrosion rate with respect to one or two different variables (such as operating temperature and shear stress or operating temperature and pH, see Figure 2.)

Generic Uncertainty Modeling Approach

An alternative approach is to apply a risk-based assessment (which sometimes includes an uncertainty, statistical or stochastic assessment). That is, the different input parameters, which are normally taken as fixed variables, are replaced with uncertain values, using distributions (instead of a single number) for the variable in the calculation. The distributions for the different parameters (flow rate, pressure, temperature, CO₂, H₂S, bicarbonate, water cut, inhibitor availability, etc.) are normally estimated based on analysis of historical variations (for an existing field) or based on engineering judgment and experience for new developments.

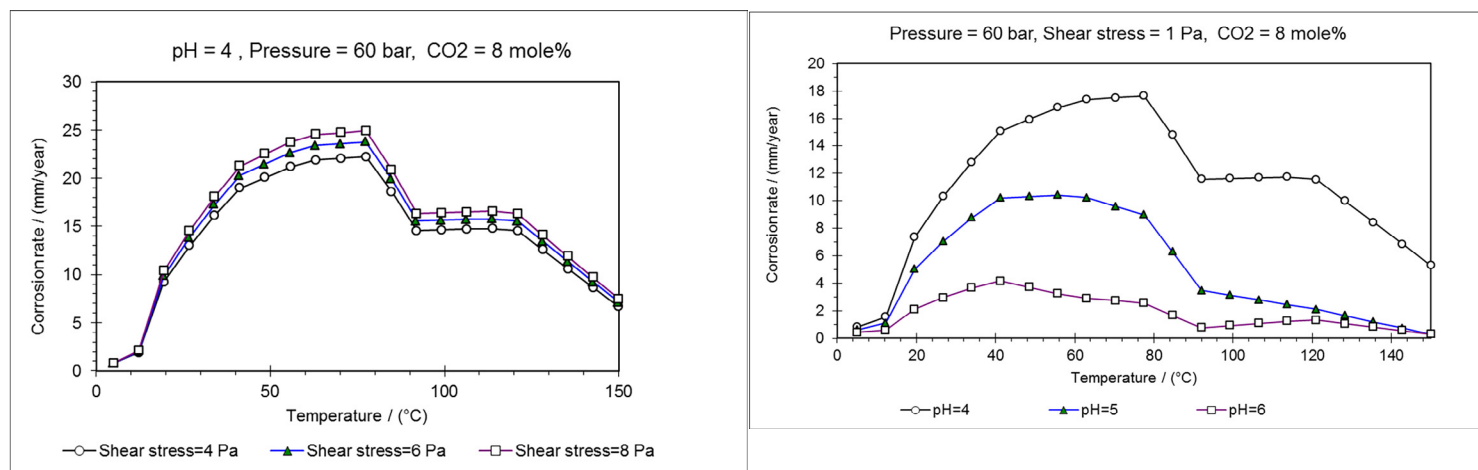


FIGURE 2: Example of Parameter Studies, Using the NO Model

⁽¹⁾American Petroleum Institute (API), 1220 L St. NW, Washington, DC, 20005-4070.

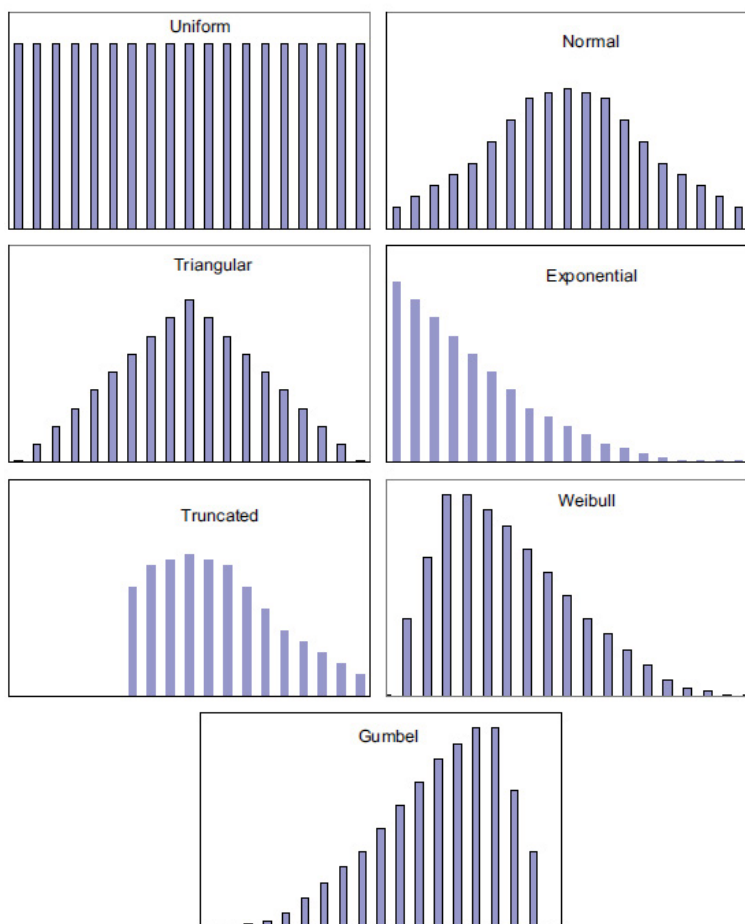


FIGURE 3: Statistical Distribution of Typical Corrosion Data⁸

With uncertainty modeling (statistical modeling), the effect of varying parameters of the predicted corrosion rate are usually quickly determined, and normally presented as a cumulative distribution graph (or S-curve).

Normally, the distribution selected for a parameter would be the "best-fit" obtained from the actual operational data collected over a period of time, which is commonly analyzed using standard distribution fitting software, often operated as an "add-in" to a computer spreadsheet. In situations where the data is insufficient to allow analysis or where operational experience is limited, the operator has to assume a suitable distribution type and range. Examples of some typical distributions found to be representative of typical oil field operating conditions are shown in Figure 3.⁸

For example, according to DNV⁽²⁾ G101, for CO₂ corrosion, a Weibull distribution is used. For localized (pitting) corrosion, the calculated value is taken as the mean, a coefficient of variance is taken as 0.45, while for general (uniform) corrosion, the mean is taken as 0.4 multiplied by the calculated value and the coefficient of variance is taken as 0.8. Pitting corrosion data sometimes exhibits Gumbel distribution (Note larger population of deeper pits).

The distributions are typically incorporated into a risk assessment analysis package (either a stand-alone package or an add-on to normal spread sheets applications), with the same formulae as would be used for a fixed value model. The difference is that instead of a single calculation, a number of runs are carried out, each with a different random variable for each parameter as determined by the particular distribution allocated to that parameter. By combining the outcome from many such runs, an overall distribution is obtained.

The most common method is the Monte Carlo simulation.⁹ The simulation calculates multiple scenarios of a model by repeatedly sampling values from the probability distributions for the different uncertain variables. During a single trial, a randomly selected value from each of the defined ranges is carried through the model to give an output. Multiple passes are carried out (typically from 1,000 to 10,000 times), which enables a range of possible outcomes to be defined. This is represented either as a histogram or a probability profile (also known as a cumulative probability curve or S-curve), an example of which is shown in Figure 4.

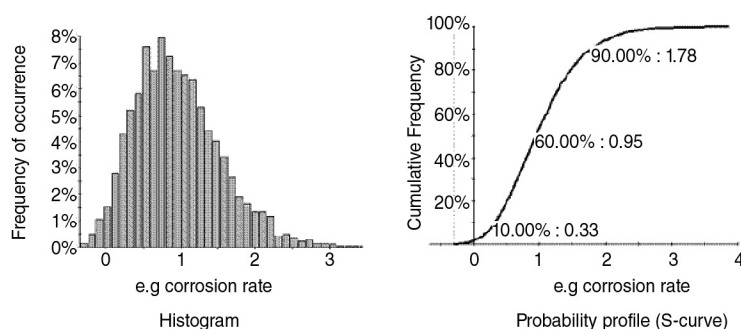


FIGURE 4: Typical Graphic presentation of Probabilistic Modeling Results

The number of runs (iterations) carried out in the analysis is dependent on calculation speed and sensitivity. Small runs (200 to 500) are normally completed almost immediately, but have a coarse output, making it difficult to discriminate at the upper (or lower) probability end. If the run is repeated, the results sometimes vary, depending on the complexity of the analysis and the size of the distributions used. Larger runs (1,000 to 3,000), while taking longer to compute, typically give a finer curve and any variation between runs in results is generally small. Very large runs (5,000 to 10,000) usually take a considerable time to complete, but provide a finer output with closely repeated results. Generally, if the critical probability desired is 90%, then 200 to 500 iterations would normally be sufficient. However, if the critical probability desired is 99%, then more than 5,000 iterations are often done.

⁽²⁾Det Norske Veritas (DNV GL), Veritasveien 1, Høvik, Norway.

The approach is typically used to combine known and unknown variables over the operational life of a facility to allow an estimate of the current condition and to then allow predictions of future condition based on different future operating scenarios (e.g., change in pigging, inhibition, new tie-ins, etc.).¹⁰

For MIC, rather than using a Monte Carlo method to estimate likelihood of failure, DNV-G101 provides an indicative probability of failure curve, based on varying operating temperature as shown in Figure 5.

Combination of Different Corrosion Threats

When considering the effect of different corrosion threats (i.e., CO₂/H₂S, MIC, oxygen, etc.) for a particular system, most methodologies first determine whether the particular threat is credible (i.e., if there is never any oxygen in the system, then oxygen corrosion does not have to be considered) and then consider them in isolation; that is, separate corrosion predictions are applied for each threat in turn.

The option then is to either consider the threat that results in the highest corrosion rate, or to combine the different threats. This is achieved in several ways: by considering a weighted average using statistical principles, or assessment of corrosion rate that considers engineering judgment and practical experience from similar fields.

For example, IF model considers that each operational parameters individually alter the pitting corrosion rates. But ultimate rate at which the pits will propagate depends on the combined effect of all of the operational parameters. Whereas the individual effect of each of the parameters can be predicted deterministically, determining the combined effect of these variables needs application of statistical principles. Except for one operational variable (i.e., water), removal or control of other variables, does not prevent pit growth although it does change the pit growth rate. The absence of water prevents pitting corrosion regardless of the effect of other variables.

Section 3: Systems Containing Only CO₂

Several prediction models for CO₂ corrosion of oil and gas pipelines are available. The models use very different approaches in accounting for oil wetting and the effect of protective corrosion films, and this accounts for much the differences between the models. Some of the models take into account a very strong effect of oil wetting for some flow conditions, while other models do not take oil-wetting effects into account at all. Some models include strong effects of protective iron carbonate films, especially at high pH or high temperature. These models rely on easy formation of protective corrosion films and absence of localized attack, while the models with weak effects of protective corrosion films assume that the films have only limited protectiveness or that there is a high risk of localized attack. All the models are capable of predicting high corrosion rates found in systems with low pH and moderate temperature, while the models predict quite different results for situations at high temperature and high pH, where protective corrosion films have the potential to form.

Several prediction models for CO₂ corrosion of oil and gas pipelines have been developed. Some of the models are mechanistically based, which include the major processes of CO₂ corrosion, while other models are simply empirical correlations of laboratory or field data. Below is a general analysis of known CO₂ corrosion prediction models available for the oil and gas industry.

Since different models were developed on different bases, different oil companies and research institutions have developed a large number of prediction models for CO₂ corrosion of carbon steel. Very different results are often obtained when the models are run for the same cases because of the different philosophies used in the development of the models. Some of the models predict corrosion rates based on full water wetting and little protection from corrosion product films. These models have a built-in conservatism and sometimes over-predict the corrosion attack. On the other hand, there is little risk that they would predict low corrosion rates for situations where corrosion problems were actually encountered in the field. Other models assume protection from oil wetting or formation of protective corrosion films. Since these models often rely on the company's field experience in conditions where the corrosion rates have been at an acceptably low level, they generally predict much lower corrosion rates.

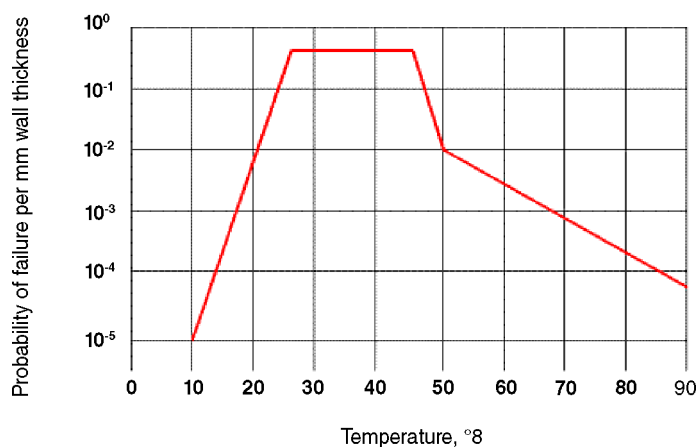


FIGURE 5: Probability of Failure Because of MIC with Respect to Temperature (from DNV-G101)⁸

Some of the models are based on mechanistic modeling of the different chemical, electrochemical, and transport processes involved in CO₂ corrosion of carbon steel. Other models are mainly based on empirical correlations with laboratory or field data. However, the mechanistic models are usually tuned against lab data to some degree, while the laboratory and field data models often have some mechanistic equations as a starting point.

The differences in predicting the effects of oil wetting and corrosion product films represent the most important differences between the various CO₂ corrosion models; while some of the models have a very strong effect of oil wetting for some flow conditions other models do not consider oil wetting effects at all. Some models include strong effects of protective iron carbonate films, especially at high pH or high temperature, while some include a qualitative risk assessment for localized corrosion attack and some do not take into any account for protective corrosion films for formation water cases because of risks for localized attack. Several models take production rates as input and use more or less simplified flow models to calculate the flow parameters, while other models take liquid flow velocity or shear stress as input without incorporating any flow modeling. Some of the models take into account top-of-the-line corrosion for wet gas pipelines with condensation of water. The water chemistry input sometimes results in large differences among the different models. All models consider dissolved CO₂, which alone causes steel corrosion. Although several of the models take the effect of H₂S or organic acid on the pH calculation into account, most of the models are not intended for use in situations where H₂S or organic acids dominate the corrosion process.

Important Factors for CO₂ Corrosion Prediction: Determination of pH

One aspect of corrosion evaluation of oil and gas wells and pipelines is to obtain a realistic estimate of the actual pH in the water phase. For cases with only condensed water, this involves an evaluation of whether the pH of the condensed water is increased as a result of bicarbonate produced by corrosion. Some of the models include bicarbonate produced by corrosion in the pH calculation. When formation water is produced, water analysis data is obtained, especially with respect to bicarbonate and organic acids. The reported pH in a water analysis is often useless for corrosion prediction, as it is usually measured at atmospheric conditions after depressurization. This gives no information about the actual pH in the pipeline, which is calculated from the CO₂ partial pressure, temperature, bicarbonate content in the water and ionic strength. Several of the models have pH modules that perform such calculations. On the other hand, some of the models show little dependence of pH on the corrosion rate, and therefore, uncertainties in the pH calculations do not have a large effect on the predicted corrosion rate. The DW, CA, HY, SW, EC, and CO models have relatively little effect of pH on the corrosion rate. The PR, SP, and SR models have relatively stronger effects of pH.

In addition to the CO₂/bicarbonate buffer system, the H₂S/sulfide and the acetic acid/acetate buffering systems are used to determine the actual pH value. The presence of acetic acid and other organic acids sometimes gives too high values for bicarbonate, hence, too high (calculated) pH values if organic acids are not measured in the water analysis.¹¹ In addition, the presence of acetic acid often has effects on the corrosion process, especially at low CO₂ partial pressures. The CO, MU, and HY models take direct account of the effect of acetic acid or other organic acids on CO₂ corrosion. The CA, KS, CP, and UL models use the organic acids only in the pH calculation, while other models ignore the presence of organic acids in the pH calculation.

In some cases, the specified water chemistry from a water analysis indicates supersaturation of calcium carbonate. One typically checks the water analysis for supersaturation of calcium carbonate at reservoir conditions, which sometimes indicate an erroneous bicarbonate analysis because supersaturation of calcium carbonate is not possible in the reservoir. In this case, the bicarbonate value is adjusted to the bicarbonate solubility at reservoir conditions with the actual calcium content. CO and MU are the only models that have a built-in check of this effect.

Effect of Protective Corrosion Films

One of the difficulties with prediction of CO₂ corrosion of carbon steel is the effect of protective iron carbonate films, especially at high temperature or high pH. At low temperatures, the iron carbonate solubility is high and the precipitation rate slow, and protective films do not form unless the pH is artificially increased. At high temperatures, the iron carbonate solubility is lower and the precipitation rate much faster, and very dense and protective iron carbonate films sometimes form. This lowers the corrosion rate from several mm/y for carbon steel without any corrosion films to less than 0.1 mm/y when protective films are present. The effect of protective corrosion films is almost considered an on/off switch, and the success of a prediction model depends to a large degree on whether it is able to predict the presence or absence of protective films or localized attack reliably, rather than on the ability to predict the general corrosion rate with certain accuracy. The picture is further complicated by the tendency to develop localized attack in the form of pits or mesa attack on steel surfaces with a partially protective film.

The effect of protective corrosion films on the predicted corrosion rate varies considerably between the models. Some of the models include very strong effects of protective films, while others include only moderate effects of protective films or do not account for protectiveness of the films for formation water cases because of the high risk of localized attack. Generally, the models with the strongest effects of protective films rely on easy formation of corrosion films with good protective properties and absence of localized attack, while the models with weak effects of protective corrosion films assume that the films have only limited protectiveness or that

there is a risk of localized attack. Some of the models predict the corrosion rate in the presence or absence of protective corrosion films together with the corrosion rate if there were no corrosion films, while some others also include a qualitative risk of localized corrosion attack. The DW, CA, HY, SW, SR, and EC models have only weak effects of protective corrosion films. The NO, CP and KS models have moderate effects of corrosion films, while the SP and PR models have very strong effects of protective corrosion films.

The worst case for CO₂ corrosion is when protective iron carbonate films are not formed, and the base case for most of the models is 100 kPa CO₂ and pure water at ambient temperature. This gives a pH value around 4 and no protective films, and it is relatively easy to predict. The differences between the models become evident at higher temperatures or higher pH, when protective iron carbonate films start to form. This is illustrated by two field data examples from the joint industry project at the Institute for Energy Technology where the different models were evaluated. The first example is a short onshore gas line with 120 kPa CO₂ partial pressure and only condensed water at a temperature of about 50 °C (122 °F). Under these conditions, protective films are typically not expected to form, and a corrosion rate of 4 mm/y was measured by ultrasonic thickness measurements. Most of the models calculated a pH around 4 for this case, and the predicted corrosion rates varied from 4 to 13 mm/y. Some of the models predicted higher corrosion rates than actually observed, and this is normally acceptable as long as none of the models failed to predict that these conditions give unacceptably high corrosion rates. The second example is an oil well with 160 kPa CO₂ partial pressure and temperature from 110 °C (230 °F) down hole to 70 °C (158 °F) at the wellhead. The formation water chemistry in this well gave pH values between 5 and 5.5, as calculated by the corrosion models. This well suffered penetrating mesa attack corresponding to 5 mm/y corrosion rate close to the top of the well, while caliper readings indicated around 0.5 mm/y corrosion rate further down in the well. The models with small effects of protective films predicted the high corrosion rates in the top of the tubing quite well, but they predicted even higher corrosion rates deeper in the well where the temperature was higher and corrosion films offered protection in practice. The models with large effects of protective corrosion films predicted the low corrosion rates in the bottom of the tubing quite well, but most of them were unable to predict the high local corrosion rates in the top of the tubing.

Effect of Oil

The influence of oil on the corrosiveness of the aqueous phase depends on a combination of three properties: (1) the emulsion of the oil and water, (2) the wettability of the steel surface, and (3) the corrosiveness of the water phase in the presence of oil (Figure 6).

Water and oil are immiscible but under certain conditions they can form emulsion. There are two kinds of emulsion, oil-in-water (O/W) and water-in-oil (W/O). W/O emulsion (in which oil is the continuous phase) has low conductivity, and is thus less corrosive; whereas O/W (in which water is the continuous phase) has high conductivity, and hence is corrosive. The percentage of water at which W/O converts to O/W is known as emulsion inversion point (EIP). At and above the EIP, a continuous phase of water or free water is present. Therefore there is a potential for corrosion.

Whether water phase can cause corrosion in the presence of oil depends on whether the surface is oil-wet (hydrophobic) or water-wet (hydrophilic). Because of higher resistance, an oil-wet surface is not susceptible to corrosion, but a water-wet surface is.

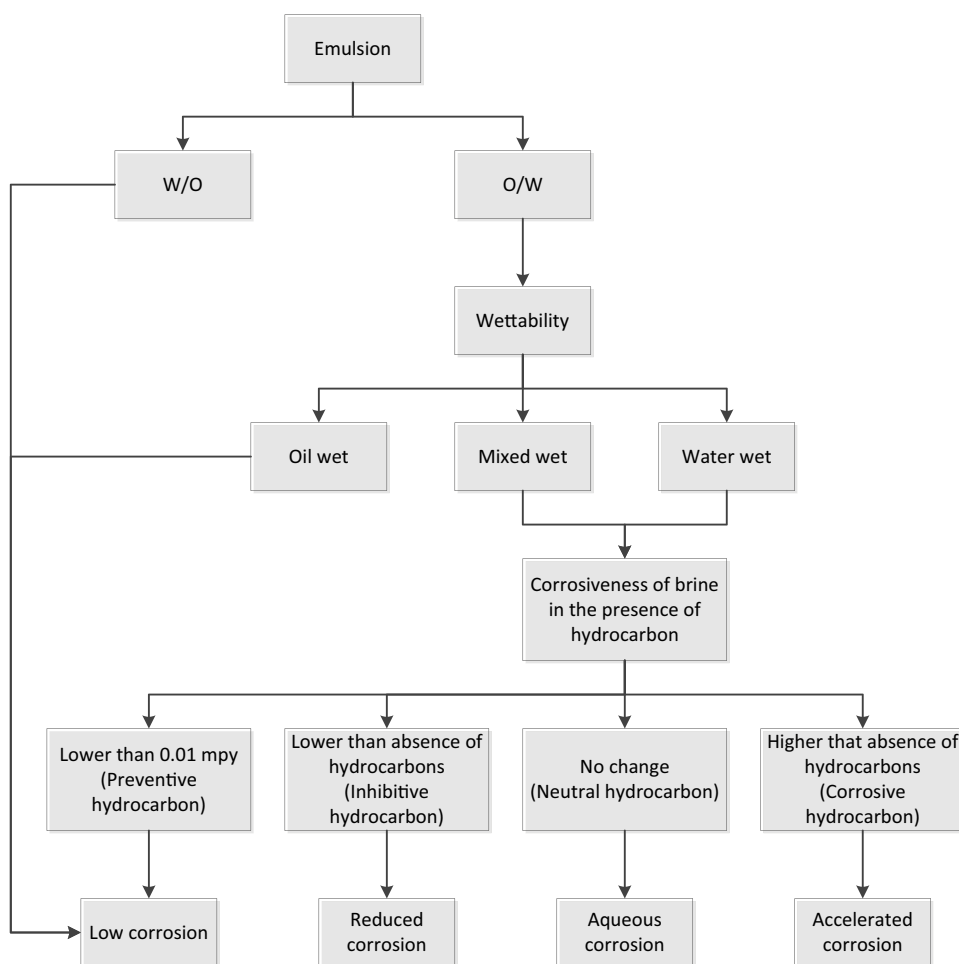


FIGURE 6: Predicting the Influence of Crude Oil on the Corrosiveness of Aqueous Phase (ASTM G205)

Dissolution of ingredients from crude oils may alter the corrosiveness of the aqueous phase. Based on how the corrosivity of the aqueous phase changes in its presence, a crude oil can be classified as corrosive, neutral, inhibitory or preventive crude.

It should be noted that emulsion (oil-water physical interaction), wettability (Steel-oil-water physical interaction), and influence of crude oil on the corrosivity of crude oil (Oil-water phase chemical interaction) are three different properties and they should all be considered in modelling the effect of crude oil on the corrosivity of aqueous phase.

Water or oil sometimes wets the steel surface, and corrosion takes place only when water is present at the surface. If the water is transported as a water-in-oil emulsion or dispersion, corrosion is often substantially reduced. The degree of oil wetting depends heavily on flow conditions, water cut, and the properties of the actual hydrocarbon, and this is difficult to assess without performing laboratory or field tests with the actual oil-water mixture. Some of the models have a very strong effect of oil wetting for some flow conditions, while other models do not consider oil wetting effects at all, either because oil wetting effects are not modelled or because it is believed that water wets the steel surface and cause corrosion somewhere in the pipeline. The NO, CA, SW, SP, SR, and KS models have no effects of oil wetting.

In the simplest form, oil wetting is considered an on/off switch in the models: either the surface is water wet with full corrosion or oil wet with zero corrosion. In the DW model, oil wetting and zero corrosion is assumed if the liquid velocity is > 1 m/s and the water cut is $< 30\%$. This effect is used for crude oil only and not for condensate, as water is considered to separate out much more easily in condensate systems.¹² In the more recent HY model, these limits are changed to 40% and 1.5 m/s, and partial protection is assumed when the water cut and flow velocity are above these limits. No protection is assumed for condensate systems.¹³ Another model is the EC model, where the oil wetting factor is dependent on the oil density, the liquid flow velocity, and the inclination of the flow.¹⁴ Oil wetting and low corrosion is assumed for a water cut lower than the emulsion breakpoint, which is calculated from the oil density and is up to 50% for heavy crude oils and close to zero for light condensate. The critical flow velocity for water dropout is taken as 1 m/s for horizontal flow and lower for inclined flow.

The CO model includes strong effects of oil wetting. The critical velocity for water entrainment in the oil is often calculated at around 0.5 m/s, and for liquid velocities above this, low corrosion rates are often predicted. The water wetting factor is dependent on the flow velocity and several other flow related parameters. The PR model also includes strong effects of oil wetting, and distinguishes between persistent and not persistent oil types.¹⁵ Low corrosion rates are typically predicted when the water cut is below 50% for highly persistent oils and 5% for not persistent oils. The UL model for gas wells has a strong effect of oil wetting when hydrocarbon condensation occurs. It typically predicts oil wetting and no corrosion for the part of the well where hydrocarbon condensation occurs, and corrosion when only water condenses. The CP model calculates a probability of water wetting depending on water cut, flow regime, local phase velocities and emulsion stability.¹⁶ In the corrosion module in the OL fluid flow model, the transition between separated and dispersed water/oil in the fluid flow model is used to determine the degree of water wetting.¹⁷ Oil wetting is assumed if oil and water are dispersed and the water cut is less than 30% , giving a dispersion with the oil as the continuous phase. The IF model considers the strong effect of crude oil based on EIP, wettability, and the influence of crude oil on the corrosiveness of the aqueous phase.

Connection with Fluid Flow Modeling

CO₂ corrosion is dependent on the flow velocity, and the models have varying degree of flow dependence. Most of the models include a simplified fluid flow calculation based on production rates and pipe diameter, while some only take flow velocity as input and use the liquid flow velocity in the well or pipeline calculated by a fluid flow model.

The IF model integrates flow, localized corrosion, MIC, and provides pitting corrosion rate, temperature, and pressure profiles along the pipeline. A corrosion module has been developed in the OG three-phase fluid flow model, where the NO model and the DW model have been combined with this fluid flow model. The CP model also represents a combination of these fluid flow and corrosion models. The HY model includes a full fluid flow model giving temperature and pressure profiles along the pipeline. The UL and DR models include flow and phase calculations along a gas well. The EC model includes a simplified flow calculation along a well or pipeline. The NO and PR models include options for point calculations of the flow parameters used in the corrosion prediction. The DW, CA, SP, SW, and KS models take liquid velocity as input calculated separately. The SR model does not account for flow effects, as temperature and chemistry data is considered much more important to the corrosion performance because of the limitations of CO₂ hydration on the corrosion process.

The variation of temperature along a well or pipeline is often much more important to corrosion behavior than variation in flow velocity and flow regime, and the effects of flow parameters on CO₂ corrosion are sometimes overemphasized. The effects of the flow parameters are the switch between oil and water wetting and the effect of flow on localized attack on surfaces covered by corrosion films, and not the effect of flow velocity on the corrosion rate itself.

Top-of-the-Line Corrosion

The discussion above concerns primarily corrosion in the bulk water phase. The situation is quite different for top-of-line corrosion, in which water condenses out in the upper part of a pipeline. The condensing water is unbuffered with low pH, but it often becomes rapidly saturated or supersaturated with corrosion products, giving rise to increased pH and the possibility of iron carbonate film formation. The top-of-the-line corrosion rate then becomes dependent on the water condensation rate and the amount of iron which is dissolved in the condensing water.¹⁸ The DW model includes a very simplified model for top-of-line corrosion, but little attention was paid to top-of-line corrosion until recently, when top-of-line corrosion was included in the HY model.^{19,20} Top-of-the-line corrosion is primarily a concern in the first few kilometers of wet gas pipelines with relatively high inlet temperatures, as the water condensation rate is rapidly reduced when the temperature difference decreases. The presence of acetic acid in gas sometimes increases the top-of-the-line corrosion rate, as it increases the amount of iron dissolved in the condensing water before protective corrosion films are formed.

Effects of H₂S

Models developed primarily for CO₂ corrosion prediction are usually not particularly suited for situations with appreciable amounts of H₂S. When even small amounts of H₂S are present, the corrosion products are iron sulfide rather than iron carbonate, since iron sulfide is much less soluble and precipitates much more rapidly than iron carbonate. Prediction models developed on the basis of formation of protective iron carbonate films are therefore not used for situations where iron sulfide films are formed instead. Some of the models use the H₂S content in the pH calculation without actually predicting sulfide-dominated corrosion, and some give a warning that the results are not valid when the H₂S content is above a certain low level, which is sometimes as low as 100–1,000 Pa H₂S. The PR model gives a marked reduction in corrosion rate because of iron sulfide films when the H₂S content is higher than about 100 Pa, the OL model indicates a reduction at even lower H₂S levels.^{21,22} The HY model uses the sweet corrosion rate multiplied with a pitting factor between 0.7 and 6 for the sulfide-dominated regime defined as $p\text{CO}_2/p\text{H}_2\text{S} < 20$. This pitting factor indicates the tendency to pitting in sulfide-dominated systems and increases with chloride content and the presence of elemental sulfur. The EC model uses a sulfide scale factor which is dependent on the HS⁻ content, which again depends on the pH. This gives a marked reduction in corrosion rate because of iron sulfide films already around 100 Pa H₂S partial pressure when the water contains bicarbonate, and less effect of sulfide films for condensed water without buffering capacity. The SR model predicted a critical ratio of H₂S/CO₂ partial pressures, above which preferential precipitation of ferrous sulfide occurs, or vice versa for ferrous carbonate.²³

The prediction of general and localized corrosion in systems with H₂S in addition to CO₂ is little developed and highly uncertain, and several of the models, but not all, give warnings stating either that the results are not valid above a certain H₂S level or that the corrosion rates in the presence of H₂S are uncertain or speculative.

Section 4: Slightly Sour Systems

Oil and gas environments that include small concentrations of H₂S have long been known to be less corrosive than similar environments without H₂S. This has been shown to be result of the rapid formation of a semi protective iron sulfide corrosion product on the metal surface. However, since there is not a procedure for determining the minimum H₂S concentration for this corrosion rate reduction, nor is there a procedure for predicting the corrosion rate, many corrosion engineers have continued to use CO₂ corrosion calculations to predict worst-case corrosion rates for this service. This has the potential to lead to excessively conservative material selections and aggressive corrosion control programs.

The following procedures provide a method for the determination of the environmental conditions for many situations in which this change from CO₂-controlled to H₂S-controlled corrosion reactions occur. A procedure is also presented to estimate worst-case corrosion rates for these low H₂S concentration (slightly sour) conditions.

To assess and predict corrosion in oil and gas production, it is helpful to define the chemistry of the corrosion reaction. In most situations, the type of corrosion product scale formed on the steel surface defines the rate-limiting step of the corrosion reaction. This scale is typically either FeCO₃, one of several forms of FeS or, on occasion, Fe₃O₄. The relationship between the type of corrosion product that forms as a function of temperature and H₂S concentration has been reported previously and is shown in Figure 7.^{24,25}

In this context, sour corrosion is a series of corrosion mechanisms that are defined by the formation of a type of FeS. There are three types of FeS that are commonly found in oilfield corrosion. These are pyrite, pyrrhotite and mackinawite. Pyrite, an ordered solid solution of FeS and elemental sulfur, is found only when elemental sulfur is present in the system. Pyrrhotite is a non-stoichiometric form of FeS that forms in most sour environments. Mackinawite is a semi-stable form of FeS that forms under the special conditions of low H₂S activity in the environment, which is referred to herein as slightly sour. The following discusses the conditions under which mackinawite is found, the chemistry of mackinawite formation, and the impact that mackinawite formation has on corrosion rates. The corrosion mechanism for higher H₂S environments, where pyrrhotite is produced, has been reported elsewhere.²⁶⁻²⁸

Slightly sour corrosion is that portion of the oilfield corrosion model, shown in Figure 7, in which the corrosion product is mackinawite. A detailed discussion of the chemical reactions that lead to the formation of mackinawite and that define the boundaries with the other corrosion products are found elsewhere. However, to summarize, mackinawite is a thermodynamically semi-stable form of FeS that forms on the steel surface under conditions in which iron sulfide is still soluble in the bulk solution; i.e., the concentrations of Fe²⁺ and H₂S are still below the saturation point of the bulk solution. Mackinawite forms instead of the thermodynamically stable pyrrhotite because the pyrrhotite formation kinetics are much slower than those of mackinawite.

The boundaries between the sweet corrosion, Fe²⁺ and FeCO₃, and mackinawite regions of Figure 7 are defined by the minimum thermodynamic activity of H₂S for the formation of FeS on the metal surface with the assumption that the Fe²⁺ activity in proximity to the metal surface is unified. The minimum partial pressure H₂S for the formation of mackinawite as the corrosion product (instead of ferrous ions) is calculated by Smith and Wright²⁶ as shown in Equation (1):

$$[pp \text{ H}_2\text{S}_{\text{vap}}] = \frac{10^{-pH \cdot 2}}{K_{\text{H}_2\text{S}_{\text{aq}}/\text{H}_2\text{S}_{\text{vap}}} * \gamma_{\text{H}_2\text{S}} * K_{\text{FeS}/\text{Fe}^2}} \quad (1)$$

Where:

[pp H₂S_{vap}] is the partial pressure of H₂S in the vapor phase at the Fe²⁺/mackinawite boundary in Figure 7.

K_{H₂S_{aq}/H₂S_{vap}} is the solubility constant for H₂S in the solution

K_{FeS/Fe²⁺} is the activity adjusted equilibrium constant for the reaction of Fe²⁺ and H₂S to form mackinawite

γ_{H₂S} is the H₂S fugacity constant in the gas phase.

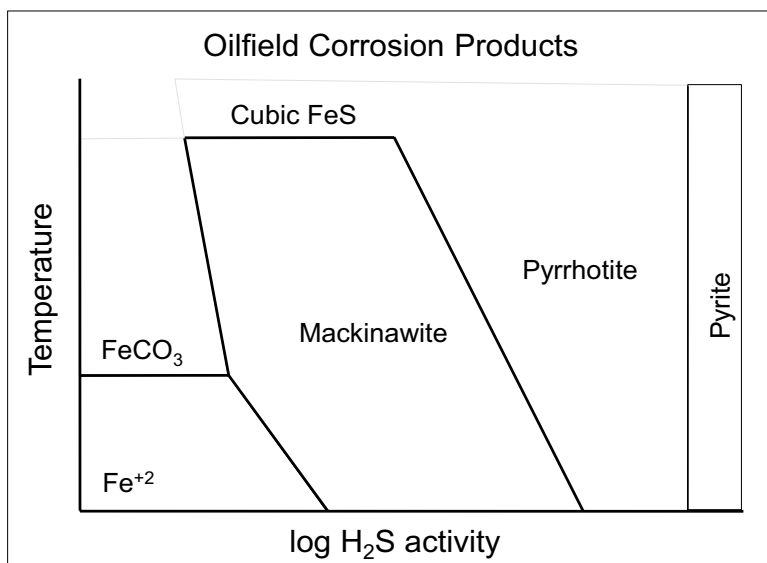


FIGURE 7: Corrosion Product Relationships

to pyrrhotite so rapidly that it is usually not detected. The problem of mackinawite detection at elevated temperature is further complicated by the addition of another metastable form of iron sulfide, cubic iron sulfide, at these temperatures. Cubic FeS, which is occasionally detected, is believed also to be an initial corrosion product formed at higher temperatures and in slightly sour exposures.

Mackinawite Properties

Iron sulfides are a very unusual class of chemical compounds that do not follow many of the intuitive concepts of the properties that a chemical salt normally possesses. For example, there is one reported amorphous form of FeS and there are eight different crystalline forms (mackinawite, pyrrhotite, pyrite, marcasite, troilite, greigite, smythite, cubic FeS).²⁹ Of these crystalline forms, only mackinawite, pyrite, marcasite, and troilite are known to exist in the proper stoichiometric ratio. The other forms, which are all varieties of FeS, do not exist with 1:1 ratios of iron to sulfur. Pyrrhotite even exists as a variable stoichiometry that is expressed as Fe_{1-x}S.

Mackinawite, pyrrhotite, greigite, and smythite are ferromagnetic. This property is important when conducting inspections of tubulars that have been corroded by H₂S. Many inspection systems rely upon magnetic flux leakage to detect wall thinning or pitting. However, since these forms of FeS are also magnetically permeable, flux leakage inspections is much less sensitive when FeS corrosion product scales are present on the tubular surface.

Identification

Although mackinawite is a common corrosion product, it is also difficult to differentiate from pyrrhotite and other forms of FeS. There are no field applicable techniques that are capable of differentiating mackinawite from pyrrhotite. In the laboratory, the only way of positively differentiating, mackinawite from pyrrhotite is x-ray diffractography (XRD). Other surface analytical techniques, such as scanning electron microscopy-energy dispersion of x-rays (SEM-EDX), secondary ion mass spectroscopy (SIMS), electron spectroscopy for chemical analysis (ESCA), and auger electron spectroscopy (AES), provide clues based on the Fe-S ratio, but are unable to positively tell pyrrhotite from mackinawite. Scanning electron microscopy and optical microscopy are normally able to detect the characteristic hexagonal crystal of pyrrhotite as opposed to the tetragonal structure of thin mackinawite tarnish films, but this is not always possible.

Although XRD is the only sure way to differentiate mackinawite and pyrrhotite, identification of mackinawite in most XRD patterns is difficult enough that many computerized XRD pattern identification programs have difficulty picking it up. Most XRD analysis is conducted with a Cu K α X-ray source. This places the major (100-level) intensity peak for mackinawite at 17.6°, which is located in the low angle scatter produced on most diffractometers. Another complication is the fact that mackinawite corrosion products occur as a very fine tarnish film on the steel surface. Fine tarnish films are characteristically extremely fine grained. Extremely fine-grained materials tend to produce peaks on XRD patterns that are broad and flat, rather than tall and sharp. Identification is difficult and could be completely disguised if a low, broad peak sits on top of a low scatter angle. Although another X-ray source would help address the problem for mackinawite, it would only complicate the matter for pyrrhotite. The 100-level peak for pyrrhotite using Cu K α occurs at 43.7°, which is not far from the pure iron peak at 44.7°. Changing to a source other than Cu K α that would move the mackinawite peak to a higher angle would also shift the pyrrhotite and iron peaks toward higher angles, in which sensitivity rapidly degrades. Therefore, from a practical standpoint, mackinawite is most commonly detected from XRD using a Cu K α source with hand interpretation of the resulting diffraction curve.

XRD analysis is also used to differentiate between the many different types of pyrrhotite listed in the XRD catalogs. The different forms of pyrrhotite are defined by long-range ordering of the missing Fe atoms in the hexagonal close packed (HCP) crystal matrix. The basic diffraction peaks generated by the base HCP structure are present in all of the patterns. It is also possible to use the XRD pattern for pyrrhotite to determine the quantity of missing Fe in the lattice. The Fe content of the pyrrhotite is determined by measuring the shift of the HCP (102) peak. Arnold and Reichen³⁰ describe the method for converting this shift into percent Fe in the pyrrhotite.

One final bit of information available from an iron sulfide XRD pattern is an indication of the degree of oxidation that has occurred in the product. Iron sulfides react with oxygen when exposed to air to form iron oxides and sulfur.



If elemental sulfur is present in the corrosive environment, the iron-sulfide corrosion product consists of a mixture of pyrrhotite and pyrite. Therefore, if elemental sulfur and Fe₃O₄ (magnetite) are present in the XRD pattern and pyrite is not, then it can be safely concluded that the FeS corrosion product was not adequately preserved prior to analysis and that some oxidation because of exposure to air has occurred.

Reactivity

As mentioned above, mackinawite is a semi stable form of FeS that tends to react quickly to form other compounds. In the region of Figure 7 where mackinawite is the corrosion product, the mackinawite is continually dissolving to form either FeS or Fe(HS)₂ ion pairs in solution. Taylor³¹ reported a description of this process. Once sufficient mackinawite has formed and dissolved to increase the appropriate Fe²⁺ ion content of the bulk solution to the saturation point, pyrrhotite precipitates on the mackinawite surface.



or



Finally, when exposed to air, mackinawite oxidizes to Fe₃O₄ and elemental sulfur by:



This oxidation is either fast or slow, depending upon the surface area of the solid and whether liquid hydrocarbons or water is wetted to the surface.

Thermodynamics of Mackinawite Formation: Mackinawite Formation Model

Equation 1 defines the minimum partial pressure of H₂S for the formation of a mackinawite tarnish layer on the surface of a piece of steel. Properties such as pH and γH₂S are specific to the particular production system.

However, the equilibrium constant values for K_{H₂Saq/H₂Svap} and KFeS/Fe²⁺ are "constants" that are dependent only upon the thermodynamic properties of the appropriate reactants and temperature. Equilibrium K values are available in tabular form for 25 °C (77 °F), or they are calculated for any temperature from the Gibbs free energy values for the reaction using Equation (6):

$$\ln K_{\text{reaction}} = \frac{\Delta G_{\text{reaction}}^T}{-RT} \quad (6)$$

Gibbs free energy values are not tabulated for reactions, but are often calculated using Gibbs free energy of formation and the concentration of the species involved in the reaction using Equation (7) shown below:

$$\Delta G_{\text{reaction}}^T = \sum_{\text{products}} G_T^0 - \sum_{\text{reactants}} G_T^0 + RT \ln \left(\frac{\prod [\text{activity}_{\text{products}}]^p}{\prod [\text{activity}_{\text{reactants}}]^r} \right) \quad (7)$$

Where G_T⁰ is the Gibbs free energy of each species at temperature T.

The difficulty with this equation is that Gibbs free energy of formation values are only available for standard conditions (25°C [77 °F] and 1 atm). There are a number of procedures that are available for adjusted Gibbs free energy values for temperatures other than 25 °C (77 °F). The procedure that has been used in this work was described by Naumov and is based upon the use of specific heat parameters to compensate for the changes in enthalpy and entropy that occur with temperature.³² The reaction for the formation of mackinawite is given as:



When the data presented in Table 1 is used to evaluate the variables in Equation (7) for the reaction in Equation (8), adjusted for temperature per Naumov and then simplified, the free energy equation for the mackinawite formation reaction becomes Equation (9) shown below:

Table 1
Reference State Thermodynamic Data for Important Chemical Species

Species	ΔH° kcal/mole	ΔS° cal/mole	ΔG° kcal/mole	CP° cal/mole-degree	a	b*10 ⁻³	c*10 ⁵
Fe	0	6.52	0	5.99	3.04	7.58	0.6
S	0	3.785	0	5.421	3.785	5.915	0.1317
H ₂	0	31.207	0	6.892	7.913	-2.75	-0.3819
FeS mackinawite	-21.968	14.5	-22.3	12.074	5.589	22.96	0.1069
FeS pyrrhotite	-25.2	14.529	-24.28	11.922	8.246	13.57	0.3413
FeCO ₃	-177	22.2	-159.35	19.63	11.63	26.792	0
H ₂ S (aq)	-9.5	29.0	-6.66	31.5	0	106	0
H ₂ S (vap)	-4.923	49.162	-7.992	8.185	6.1997	5.247	0.3894
Fe ²⁺	-22.05	-25.3	-21.87	7.9	0	26.5	0
H ⁺	0	0	0	0	0	0.	0

$$G_{\text{reaction}}^T = 961.1 + 93.473 \times T - 11.297 \times T \times \ln(T) - .135 \times T^2 - \frac{4.196 \times 10^5}{T} + \frac{2.147 \times 10^7}{T^2} + 0.0196 \times T^2 \times \ln(T) + 7.2 \times 10^4 \times \frac{\ln(T)}{T} + RT \times \ln\left(\frac{\Pi(\text{activity})^p}{\Pi(\text{activity})^r}\right) \quad (9)$$

Where T is in °K.

Since the activity of a solid, such as FeS, is assumed to be 1, and assuming that the activity of ferrous ions near or on the surface of the metal approaches a value of 1.0, Equation (1) is simplified and rearranged to form Equation (10):

$$\log(\text{activity } H_2S) = pH \times 2 - \frac{\Delta G_T^0}{R \times T \times \log(10)} \quad (10)$$

Where:

$$\Delta G_T^0 = 961.1 + 93.473 \times T - 11.297 \times T \times \ln(T) - .135 \times T^2 - \frac{4.196 \times 10^5}{T} + \frac{2.147 \times 10^7}{T^2} + 0.0196 \times T^2 \times \ln(T) + 7.2 \times 10^4 \times \frac{\ln(T)}{T} \quad (11)$$

Equations (10) and (11) are then combined, rearranged, and simplified into Equation (12) shown below. This equation assumes that the activity of H₂S is in equilibrium between the gas and liquid phases. This assumption allows the more readily available value of H₂S partial pressure in the gas phase to be considered. A similar value could be derived that would consider H₂S dissolved in the solution. However, a solution H₂S-based equation would be much more complex, since determination of an activity coefficient for H₂S in the water instead of the fugacity correction for non-ideality of the gas would be used.

$$ppH_2S = \frac{10^{\frac{\Delta G_T^0}{4.575 \times T} - 2 \times pH}}{\gamma} \times P \quad (12)$$

Where:

ppH₂S = Minimum partial pressure of H₂S for the formation of mackinawite

γ = Fugacity coefficient for H₂S in the gas phase

P = System pressure

T = Temperature

ΔG° = Gibbs free energy

It is critical to point out that the pH value that is used in this calculation is the pH of the corrosive water at the temperature and pressure of exposure. This value is dependent upon the amount of CO₂ and H₂S dissolved in the water, which usually drops sharply once pressure on the sample is relieved. The difference between a pH value of a water sample measured at room temperature and pressure and in downhole tubing string or pipeline pH is sometimes greater than 2 pH units. Since the effect of pH on the critical H₂S value is 10⁻²*pH, an error of 2 pH units means an error in the critical H₂S value of 10,000 times. Similarly, the effect of the fugacity constant for H₂S, γ_{H₂S}, is not typically ignored. This value is a range from 0.4 to 1.0, therefore more than double the amount of H₂S.

Mackinawite and Iron Carbonate

The preceding equations define the boundary between the mackinawite and the ferrous ion regions shown in Figure 1. When mackinawite is being formed, the ferrous ion region extends to higher temperatures than expected when the corrosion products would normally be Fe²⁺ and FeCO₃. This is because of the very rapid kinetics of mackinawite formation and the fact that the mackinawite consumes or complexes most of the Fe²⁺ ions produced by the corrosion reaction. This consumption of Fe²⁺ ions keeps the Fe²⁺ concentration low and thereby retards FeCO₃ precipitation. Since this is a kinetic consideration, it is not reflected in Table 1.

However, at some degree of elevation of temperature, the corrosion product is usually expected to change from Fe^{2+} to FeCO_3 . The simple H_2S partial pressure vs. pH relationship given in Equation (12) is therefore modified to reflect the formation and stability of FeCO_3 .

Dunlop proposed a simple order-of-magnitude correlation of the $\text{CO}_2/\text{H}_2\text{S}$ partial pressure ratio to define the coexistence of FeCO_3 and all forms of FeS .³³ Based upon tabulated data at 25 °C (77 °F), and specifically ignoring temperature and solution effects, Dunlop determined that FeCO_3 would be the corrosion product if the partial pressure ratio is greater than 500 and that FeS would form if the ratio was less than 500.

Since Dunlop was looking at conditions where both iron carbonate and sulfide were stable, he described a very simple way to define the FeCO_3 /mackinawite boundary found in Figure 7. Smith reported a more detailed version of this equilibrium boundary could be defined by Equation (13):

$$K_{\text{FeS/FeCO}_3} = \frac{(a_{\text{H}_2\text{O}} \times K_{\text{CO}_2\text{aq/CO}_2\text{vap}} \times a_{\text{CO}_2\text{vap}})}{(K_{\text{H}_2\text{CO}_3\text{aq}} \times K_{\text{H}_2\text{Saq/H}_2\text{Svap}} \times a_{\text{H}_2\text{Svap}})} \quad (13)$$

Where:

a values are activities of the various species

K values are the equilibrium constants

This relationship is simplified by combining the equilibrium constants into a single constant and making the simplifying assumption that the activity of water is equal to 1.0, to produce an equation that is very similar to the one reported by Dunlop as shown in Equation (14):

$$K_{\text{FeS/FeCO}_3} = C \times \frac{a_{\text{CO}_2\text{vap}}}{a_{\text{H}_2\text{Svap}}} \quad (14)$$

Therefore, using the thermodynamic procedures and data described above and in Smith, it is possible to extend Dunlop's value of for the FeCO_3/FeS value of $C = 500$ beyond the 25 °C (77 °F) and ideal gas assumption to most any temperature and to non-ideal gas conditions.

Mackinawite and Pyrrhotite

The boundary between the mackinawite region of Figure 7 and the pyrrhotite region is defined by the solubility of FeS in the bulk solution. When FeS is below the saturation limit in the bulk fluid and H_2S is greater than the level for mackinawite formation, mackinawite is the corrosion product. When the FeS levels in the bulk fluid meet or exceed saturation levels, pyrrhotite is the corrosion product. The boundary between these two corrosion model domains is therefore defined by the same series of equations as Smith and Wright used to develop Equation 1. The one exception is that the simplifying assumption that the iron ion activity on the surface of the metal $\square 1.0$ is replaced by a term to consider the activity of ferrous ion in the bulk solution. The resulting Equation (15) therefore takes the form:

$$\left[\text{pp H}_2\text{S}_{\text{vap}} \right] \times \left[\text{activity Fe}^{+2} \right] = \frac{10^{-\text{pH} \times 2}}{K_{\text{H}_2\text{S}_{\text{aq}}/\text{H}_2\text{S}_{\text{vap}}} \times \gamma_{\text{H}_2\text{S}} \times K_{\text{FeS/Fe}^{+2}}} \quad (15)$$

Where:

$[\text{activity Fe}^{2+}] = \gamma_{\text{Fe}^{2+}} \times m_{\text{Fe}^{2+}}$,

$\gamma_{\text{Fe}^{2+}}$ = activity coefficient of Fe^{2+} for solution at the temperature and pressure of the exposure conditions

$m_{\text{Fe}^{2+}}$ = molal concentration of Fe^{2+} in the solution.

It is important to include the activity coefficient in the calculation since, in many cases, the value for $\gamma_{\text{Fe}^{2+}}$ is around 0.1. Ignoring the activity coefficient and simply using the concentration of Fe^{2+} introduces an error that increases the apparent minimum Fe^{2+} concentration for pyrrhotite formation by a factor of 10.

Comparing Equation (15) to Equation (1), one sees that the boundary between mackinawite and pyrrhotite is a function of the same factors as the ferrous ion-mackinawite boundary. The difference is the consideration of the Fe^{2+} activity in the bulk solution and its contribution to the conditions that lead to mackinawite dissolution and pyrrhotite stability. This means that the pyrrhotite boundary is calculated by adapting Equation (12) through the addition of the ferrous ion activity value.

Mackinawite Corrosion Model

The preceding sections discussed the conditions under which a mackinawite tarnish film forms. Unfortunately, this reaction has nothing to do with the rate of the corrosion reaction, other than it serves as a prerequisite. The rate-controlling step in the slightly sour corrosion reaction is the dissolution of the mackinawite. Mackinawite is the corrosion product that only forms under conditions where the Fe^{2+} and H_2S concentrations in the bulk solution are still low enough that FeS is under saturated and is therefore still soluble. If FeS is still soluble in the bulk solution, then any tarnish film that forms on the metal surface tends to dissolve. The only reason that a visible tarnish film even exists is that the FeS formation reaction is exceedingly fast and the dissolution step is slow.

Dissolution of mackinawite generally occurs by one of several reactions, depending upon the form that the dissolved FeS takes. A typical reaction is:



FeS and H_2S form a number of different complexes, ions and ion pairs in solution, depending upon the pH and the Fe^{2+} and H_2S concentrations. Some of these include:

- FeS (ion pair)
- $\text{Fe}(\text{HS})^+$
- $\text{Fe}(\text{HS})_2$ or $\text{FeS} \cdot \text{H}_2\text{S}$
- FeHS_2^- or $\text{FeS} \cdot \text{HS}^-$
- FeS_2^{2-} or $\text{FeS} \cdot \text{S}_2^-$
- Fe^{2+}

The reaction rate for the dissolution of mackinawite is expressed in Equation (17):

$$\text{Rate} = k \times 10^{-\text{pH}} \times [\text{FeS}] \quad (17)$$

Where:

k = the reaction rate constant (which is a function of temperature), and $[\text{FeS}]$ = the molar concentration of solid FeS , which is defined as 1 for a solid species.

Tewari³⁴ measured the iron ion release rate from a dissolving mackinawite surface in a series of experiments at various flow rates and two temperatures. He was then able to extrapolate this data to infinite flow rate to remove any consideration of iron ion complex diffusion. This allowed values for k to be determined at two temperatures, which therefore allowed the activation energy and rate constant for the reaction to be determined.

Since mackinawite dissolution determines the corrosion rate, these values are used to determine a worse case corrosion rate for environments that produce mackinawite. Actual corrosion rates are less than this value since the equation assumes infinite flow rate, but often the calculated rate is less than a De Waard and Williams³⁵ calculation for related conditions. The corrosion rate equation that is derived is a function of pH and temperature, in °K in Equations (18) and (19):

$$\text{CR} = e^{\frac{-9255}{T}} \times 10^{-\text{pH}} \times 2.302 \times 10^{19} \text{ mpy} \quad (18)$$

or

$$\text{CR} = e^{\frac{-9255}{T}} \times 10^{-\text{pH}} \times 5.848 \times 10^{17} \text{ mm/y} \quad (19)$$

Tewari provided the information used to predict the dissolution rate and also measured the value of the diffusion constant for predicting the diffusion rate.³⁶ This was done by performing rotating disk tests to study the effects of increasing flow velocity. He reported: "The total corrosion (metal loss) increases significantly with the speed of rotation, but the amount of iron sulfide scale remaining on the disk is almost independent of the rotation speed." These results show that the dissolution or the dispersal of the iron sulfide film from the carbon steel disc is accelerated by an increasing fluid velocity, but this is balanced by the formation of a fresh iron sulfide film on the disc surface with increased corrosion. The rate of formation of iron sulfide film on the carbon steel surface is almost instantaneous."

Unfortunately, Tewari's testing was not designed to provide the type of data for modeling fluid flow in a manner such as has been studied for CO₂ corrosion. Hopefully, the extension of the CO₂ flow effects research effort to the study of the diffusion of mackinawite dissolution products allow slightly sour flow effects to be modeled in the near future.

Conclusions

Based upon the information contained in the preceding pages and in the work by Smith and Smith and Wright, it is possible to conclude:

- It is possible to explain variations in field corrosion experience that occur with varying small concentrations of H₂S.
- It is possible to predict minimum H₂S levels for slightly sour corrosion to occur from basic thermodynamic principles.
- The proposed slightly sour corrosion mechanism is consistent with laboratory test results.
- Although it is possible to predict corrosion rates for slightly sour conditions, the predictions are currently unreliable in regards to defining velocity effects.

Section 5: Systems Containing Appreciable H₂S

Hydrogen sulfide (H₂S) naturally occurs in some gas and crude oil reservoirs. H₂S is also generated by sulfate-reducing bacteria (SRB). H₂S, when dissolved in water, is a weak acid. In the absence of buffering ions, water equilibrated with 1 atm of H₂S has a pH of about 4. Under high-pressure, however, pH values as low as 3 have been calculated.³⁷

Corrosion of carbon steel or iron in H₂S solution leads to the formation of an iron sulfide layer. The formation of iron sulfide films can proceed either by reaction of H₂S with the metal surface or with air-formed iron oxides, as shown below in Equations (20) and (21):



Iron sulfide (FeS) is protective. Once formed uniformly, it reduces the corrosion. However, there are several types of FeS surface layers, such as pyrrhotite, troilite, mackinawite, marcasite, pyrite, and geoigite. The relationship between FeS type or morphology of surface layers and corrosion is not well understood.³⁸

At high H₂S partial pressure, sulfanes (free acid form of polysulfide) are formed in the gas phase by the dissolution of elemental sulfur. During the transportation of sour (H₂S) gas in the production pipelines, the sulfanes dissociate and elemental sulfur precipitates. In the aqueous phase, under acidic conditions, sulfanes dissociate into H₂S and elemental sulfur. Elemental sulfur can also be formed by the oxidation of H₂S by air or by oxides (for example, iron oxides), as shown below in Equations (22) and (23):



This oxidation is detrimental for two reasons. First, it produces water, which causes dry H₂S, (which is non-corrosive) to become corrosive. Second, it yields wet elemental sulfur, which causes severe sulfur corrosion.^{39,40}

The solubility of S⁰ in water is ~10 ppm to 20 ppm at 25 °C (77 °F), increasing to 50 ppm at ~50 °C (122 °F).⁴¹ Dissolution of sulfur in water yields H₂S and sulfuric acid, as shown below in Equation (24):



Sulfur is a powerful oxidant for organic and inorganic materials. The presence of sulfur tremendously increases the sour corrosion rate.

The presence of H₂S sometimes leads to cracking and localized pitting corrosion. The occurrence of both cracking and corrosion in sour oil and sour gas production started in the 1950s. In many wells, replacement of broken sucker rods and completely perforated tubing has been done at frequent intervals. In some cases, the intervals have been 30 days or less, either because of corrosion products from the pipe accumulating in the pump or as a result of corrosion failures of pipelines.

NACE MR0175/ISO⁽³⁾ 15156⁴² provides guidelines on mechanisms and modeling of cracking. It also provides guidance for selection and qualification of metallic materials (carbon steels and corrosion-resistant alloys [CRAs]). Specific standards are also available to carry out laboratory tests to select and qualify materials with respect to SSC (NACE TM0177)⁴³ and HIC (NACE TM0284)⁴⁴. Almost all materials for sour oil and gas service are routinely selected and qualified using these standards. Additional guidelines for selecting materials without cracking in sour environments are provided in NACE SP0472,⁴⁵ NACE 8X194,⁴⁶ NACE SP0296,⁴⁷ API 944,⁴⁸ and API 950⁴⁹.

On the other hand, scientific knowledge with respect to sour corrosion has not yet matured to the level of our knowledge on cracking in sour environments. However, some of the current understandings are summarized here.⁵⁰⁻⁵⁴

Because iron sulfides have low solubility, rapid precipitation, and good mechanical properties, velocity effects are generally not encountered in sour systems at velocities up to 30 m/s (100 ft/s).

- The formation of FeS₂ on the surface is promoted by 20% cold-working, resulting in a decrease in corrosion.
- At temperatures between 150 and 230 °C (300 to 450 °F) and H₂S partial pressures (1,000 psi) encountered in deep sour gas wells, a barnacle type of localized corrosion occurs. This type of attack is promoted by polysulfide-type species and the presence of a minimum chloride concentration. This mechanism operates at lower rates under much milder conditions. In the barnacle mechanism, corrosion is sustained beneath thick but porous iron sulfide deposits (primarily pyrrhotite, FeS_{1.15}) because the FeS surface is an effective cathode.
- Pitting of steel in H₂S solutions occurred in the presence of chlorides on steel having a black oxide surface (mill scale). Pitting occurs between pH 3 and 6. General corrosion occurred at pH 2 or lower.
- Pitting corrosion occurred on horizontal surfaces in the crude carrier tanks. The primary chemical involved is H₂S in the crude oil. The H₂S creates a strong reducing environment during the time the tank is filled with crude oil. The H₂S reacts with iron to produce iron sulfide, which is strongly cathodic to steel. Iron sulfide is oxidized during the washing phases and forms magnetite, which is also cathodic to steel. The oxidation-reduction cycle involving air, seawater, oil, and hydrogen sulfide provides a mechanism for pitting corrosion experienced on horizontals in sour crude oil ships.⁵⁵

The effect of H₂S on pitting corrosion rate is determined by the formation and stability of iron sulfides. Iron sulfides are generally good electronic conductors and have a low overpotential for hydrogen evolution and defective structures. The experimentally determined variation in pit growth rates with H₂S partial pressure, based on 100 h of high-pressure laboratory tests is presented in Table 2.⁵⁶

Table 2
Effect of Partial Pressure of H₂S

Partial pressure H ₂ S, psi	Pit growth rate, mpy
< 2.5	85
2.5 to < 10	50
10 to < 50	45
≥ 50	40

Table 3
Summary of Localized Pitting Corrosion Rates in Sour Oil and Gas Production Fields

Field	H ₂ S partial pressure, psi	Deepest pit (mil)	Test duration, days	Maximum pitting corrosion rate, mpy	Predominant surface layers	
					Composition	% Composition
A	0.1	21	479	18	FeCO ₃	46
B	2.0	9	1,439	2	–	
C	2.0	6	1,250	2	FeS	37
D	2.0	106	1,449	27	FeCO ₃	11
					FeO(OH)	17
					FeS	13
					Fe ₃ S ₄	16
E	0.1	11	1,099	11	FeOOH	23
					SiO ₂	46
F	0.1	63	1,357	17	FeCO ₃	55
					FeO(OH)	23

Based on field tests conducted in six operating sour oil and gas production pipelines over a period of four years, a study found that pitting corrosion rates were similar when the compositions of surface layers were similar. When a compact layer of single species formed, the surface was protected from pitting corrosion. The FeS layer was more protective than the FeCO₃ layer. When multiple layers of several species formed, the susceptibility of the surface to pitting corrosion rate increased. Frequent changes in the pipeline operating conditions facilitated formation of multiple layers as shown in Table 3.⁵⁷

⁽³⁾International Organization for Standardization (ISO), 1 Ch. de la Voie-Creuse, CP 56, 1211 Geneva 20, Switzerland.

Predicting Sour Corrosion

Papavinasam et al developed an empirical sour corrosion model based on high pressure laboratory tests carried out under simulated conditions representing Canadian conventional oil and gas production conditions, field tests in six operating sour oil and gas production pipelines, and analyzing 40 years of oil and gas production corrosion data. According to the model, the localized pitting corrosion rate (PCR_{H_2S}) varies with H_2S partial pressure (in the range 0 to 50 psi) as:⁵⁸⁻⁶³

$$PCR_{H_2S} = -0.54p_{H_2S} + 67 \quad (25)$$

Section 6: Microbiologically Influenced Corrosion (MIC)

General Considerations

Microbiologically influenced corrosion (MIC) occurs when a unique combination of biological factors is present simultaneously with other conditions, such as specific regimes of water chemistry, temperature, flow velocity, metallurgy, and organic and inorganic fouling materials. The biological factors involve formation of biofilms that influence the corrosion mechanism (usually a biofilm contains both aerobic autotrophic bacteria and anaerobic autotrophic/chemolithotrophic bacteria). These microorganisms are associated with MIC.

This report briefly describes the types of microorganisms involved in MIC, methods to monitor them, and models to predict the occurrence and risk of MIC.

Microorganisms

A wide diversity of microorganisms are found in hydrocarbon reservoirs, and in oil and gas production and transportation systems. Microorganisms are typically classified according to their metabolic processes. For the purposes of the following section, the state in which the microorganisms are found in oil and gas systems is used. The terms "planktonic", and "sessile" are used to describe bacteria that are flowing with the production fluids, or stationary on a fixed surface, respectively.

Planktonic Microorganisms

Free-floating bacteria are commonly referred to as planktonic microorganisms, but depending on the type of industrial system, unattached algae, diatoms, fungi and other microorganisms are sometimes present in bulk fluids. In most cases, it is planktonic bacteria that are the focus of monitoring for MIC, since system fluids are generally easier to sample than metallic surfaces. Unfortunately, the levels of planktonic bacteria present in the liquids are not always indicative as to whether MIC can occur or, if so, to what extent. At best, detection of viable planktonic bacteria serves only as an indicator that living microorganisms are present in a particular system. Only those microorganisms capable of participating in a microbial attack of materials, such as sessile sulfate reducing bacteria (SRB), are typically monitored. Monitoring of planktonic microorganisms is sometimes misleading. Table 4 shows a comparison between plank-

Table 4
Quantification of Planktonic and Sessile Bacterial Population

Point of sampling	Microbiological Analysis	
	Planktonic Sulfate-Reducing Bacteria (cell/mL)	Sessile Sulfate-Reducing bacteria (cell/cm ²)
APP-21/M-UD-AY	10 ¹	2x10 ⁷
MPP/ICB	10 ²	2x10 ³
RN-3/MRN-1 UD-518	10 ¹	2x10 ⁵
RN-04/M-UD-4 UD-531	10 ¹	2x10 ²
RN-11/UD-111 UD- 673	10 ¹	2x10 ⁴
EF-UD-7/APP21	10 ¹	2x10 ⁴

tonic and sessile SRB counts for different submerged crude oil transport pipelines in a saline lake.⁶⁴ The situation is more critical and costly if a biocide treatment is performed based on the evaluation of planktonic bacteria. For example, following biocide application, elimination or reduction of viable planktonic organisms implies to many operators a successful treatment program, whereas in reality, attached organisms are sometimes unaffected by the biocide treatment and are capable of continuing their attack on metal surfaces.

Sessile Microorganisms

Microorganisms that are attached to a surface are termed sessile microorganisms. Bacteria and other microorganisms are almost always present as a consortium or community of organisms, collectively referred to as a biofilm. Since MIC occurs directly on metal surfaces, sessile organisms are the ones that are most representative of potential problems and, therefore, are an important component to monitor. Monitoring sessile microorganisms in systems or pipelines are usually either regularly opened for sampling or accommodations are made in the system design to allow for regular collection or on-line tracking of attached microorganisms during operation. NACE Standard TM0194 is used to monitor the sessile bacteria.

MIC Models

Six MIC indexes, or models, that have been developed and published during the past decade are described in the following paragraphs.

Sooknah Model

The Sooknah model assumes boundary conditions in which MIC occurs and then provides quantitative scores for the risk of MIC.^{65,66}

The conditions, in which MIC occurs, as assumed by the Sooknah model, are as follows:

- The temperature is between -10°C (14°F) and 120°C (248°F).
- The metallic surface is water-wet
- Organic/inorganic nutrients for the development of microorganisms are available
- No antifouling procedures are regularly applied

All bacteria proliferate in water phase. If any minute amount of water wets the metal surface or deposits attached to the metal surface, biofilm formation is likely.

- In the absence of water, MIC does not occur
- In the presence of water, the model predicts the likelihood of MIC

The risk of MIC depends on nine parameters (temperature, flow rate, pressure, pH, Langelier Saturation Index (LSI), total suspended solids (TSS), total dissolved solids (TDS), redox potential (Eh), and sulfur content in solids). Each parameter is assigned a numerical value between 0 and 10, except for flow rate, which is assigned a numerical value between 0 and 20. Values approaching 0 signify low MIC risk and values approaching maximum signify higher MIC risk. The MIC risk factor (RF) is calculated as the sum of risk factors of all nine contributing parameters. The numerical risk factor of individual parameters is presented in Table 5.

Pots Model

The Pots model predicts occurrence of MIC by considering:⁶⁷

Table 5
Risk Scores for MIC in the Sooknah Model

Influence of Parameter	Range of Parameter	Unit of Parameter	MIC Risk Score (Value of F)	Remarks
Temperature	< -15	$^{\circ}\text{C}$	0	
	-10 to 15		1	
	15 to 45		7 to 10	
	45 to 70		4 to 7	
	70 to 120		1 to 4	
	Above 120		0	
Pressure	> 20	$\text{pCO}_2/\text{pH}_2\text{S}$	10	Only if gas contains H_2S greater than 10 mole/kilomole (1%) by volume
	< 20		2	
Flow rate	Above 3	m/s	1 to 2	
	2 to 3		2 to 12	
	1 to 2		12 to 18	
	0 to 1		18 to 20	
pH	< 1		0	
	1 to 4		5	
	4 to 9		10	
	9 to 14		1	
	Above 14		0	
Langelier Saturation Index (LSI)	< 0		10 to 5	MIC tendency decreases as the LSI value increases in the negative direction because the tendency of non-MIC increases.
	0		0	
	> 0		1 to 8	MIC tendency increases as the LSI value increases as more scales are formed.
Total Suspended Solids (TSS)	Present		10	If the flow rate is between 0 to 3 m/s.
	Present		0	If the flow rate is above 3 m/s
	Absent		0	
Total Dissolved Solids (TDS)	< 15,000	ppm	1	
	15,000 to 150,000		1 to 10	
Redox potential (Eh)	-15 to 150	mV	10	
Sulfur content in solid	Present		10	ASTM ⁽⁴⁾ D 4294
	Absent		1	

⁽⁴⁾ASTM International (ASTM), 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA 19428-2959.

1. Environmental conditions supporting microbial activity and biofilm formation.
2. Operational parameters influencing microbiology

The MIC rate is calculated using Equations (26) and (27):

$$MR = Cx F^p \quad (26)$$

$$F^p = f_1 \cdot f_2 \cdot \dots \cdot f_n \quad (27)$$

Where:

MR is the MIC rate

C is a constant (assumed to be 2 mm/y)

p is a power laws index (assumed to be 0.57)

f are factors influencing MIC.

Maxwell and Campbell Model

Maxwell and Campbell modified the Pots MIC model for the following reasons:⁶⁸⁻⁷³

- The model does not include influence of SRB cell numbers, SRB growth rates, sulfide production, and water content.
- The model over-predicts the influence of pigging operations on MIC.
- Formation of corrosive biofilm is a first step for MIC to occur.
- There is a lag period before biofilm develops, and the lag period varies depending on several parameters.
- Not all biofilms lead to corrosion
- Abiotic corrosion (i.e., corrosion takes place because of non-microbial activity) sometimes occurs concurrently with biotic corrosion; therefore, they have a combined influence.

CW Predictive Model

The CW model provides guidelines when dealing with the prevention of MIC. It serves as a guide to define and compare the potential for MIC at different locations⁷⁴⁻⁷⁷. This model provides a susceptibility ranking of components or specific sites in, e.g. piping, elbows, welds, heat exchanger tubes, tube sheets, pumps, valves, etc. A ranking is made of the susceptibility or extent of the potential for MIC to occur under the conditions used to calculate the ranking. The ranking is from 0 (no susceptibility or very low potential) to 10 (highest susceptibility or greatest potential for occurrence of MIC). The model is mathematically expressed in Equation (28):

$$\text{Susceptibility to MIC} = (MWF \times TF \times OF \times BF \times BD \times DF)^{1/3} \quad (28)$$

Where:

MWF (Materials - Water Factor) accounts for interaction of material of construction with water of known chemistry

TF (Temperature Factor) accounts for the change in corrosiveness of the water and associated corrosion rate related to temperature

OF (Operation Factor) accounts for the component being exposed to continuous, intermittent, or stagnant flow conditions

BF (Biocide Factor) accounts for the use of biocides to control microbiological growth, and accounts for the change in effectiveness of various biocides as related to water chemistry, e.g. pH, and suspended solids

BD (Biocide Decay Factor) accounts for loss of effectiveness of biocide with distance under actions of organic carbon and sulfides

DF (Discontinuity Factor) accounts for the increased susceptibility at discontinuities in construction such as at welds and crevices

1/a is a constant

Union Electric Callaway MIC Index (UE)

The UE model provides a relative indicator for the likelihood of MIC to be occurring in a system or individual component at the time that the test data are obtained.⁷⁸⁻⁸⁰ It is actually an attempt to assess the potential degree of severity of MIC under existing conditions. The index is modeled on values obtained from data collected over a period of time at sites that were inspected and tested, and where the level of MIC actually observed was rated as low, moderate, severe, or very severe (component failure).

The index is measured on a scale of 0–100, a rather broad range to account for variations inherent to making subjective estimates of the degree of susceptibility or severity of MIC by visual interpretation. The broad range also accounts for inherent procedural variability that is associated with making microbiological cultures from samples obtained at the sampling site. This index places great significance on the impact of microbiological growth at the site where samples are obtained and where visual examination is made. The index is expressed mathematically in Equation (29):

$$Index\ Value = 4.5446[929 - SRB)/4.83 + (6 - Clos) + (9 - Gall)/1.5 + Silt\ Factor + Visual\ Factor \quad (29)$$

Where:

SRB is the number of days for sulfate reducing bacteria cultures isolated from samples to turn positive

CLOS is the number of days for Clostridia cultures isolated from samples to turn positive

GALL is the number of days for Gallionella cultures isolated from samples to turn positive

Silt Factor represents the amount of sludge/silt present at the sampling site (0 = no silt) (1 = moderate amount of silt) (3 = high amount of silt)

Visual Factor represents a visual estimate of the amount of deposit or tubercle formation at the sampling site (0 = few or none); (1 = moderate soft tubercles/deposit); (3 = many large hard tubercles/deposits))

4.83 is a factor to weigh evenly SRB to CLOS

1.5 is a factor to weigh evenly Silt/Visual to SRB/CLOS/GALL factors

4.5446 is a factor to correct calculation to worst case of 100

The index values are:

- 0 to 25: Low potential/low degree of severity
- 26 to 50: Moderate potential/moderate degree of severity
- 51 to 75: High potential/high degree of severity
- 76 to 100: Very high potential/very high degree of severity

Lutey/Stein MIC Index (L/S)

The L/S index also places significant emphasis on the presence of specific bacteria associated with corrosion that is induced or influenced by the growth of those bacteria.⁸¹ The viability or aggressiveness of growth of the microbiological community, rather than the numbers of individual types of bacteria in the microflora, is considered more important. This premise eliminates variables associated with specific environmental conditions, such as pH, temperature, O₂, and nutrient availability. The viability of the microflora and the ecology of the specific bacteria respond to those environmental conditions and reflect their effect by the presence or lack of aggressive growth. A baseline level of microflora viability is developed by making numerous microbiological surveys of the system over an extended period. Microbiological data relating to four specific groups of bacteria constitute the baseline information. These are SRB, slime-forming bacteria, metal oxidizing bacteria, such as *Gallionella sp.* and manganese oxidizing bacteria, and acid producing bacteria, such as *Clostridium sp.* The data input used to calculate the index have the potential to be affected by the presence of other bacteria and contribute to MIC.

Other criteria included in the L/S MIC Index are the deposit/fouling factor, sedimentation factor, and materials of construction factor. These factors are considered significant because they are directly involved in the mechanisms associated with the degradation or corrosion of the component. They also affect the microenvironment where the microorganisms exist.

Because sampling site and sampling frequency for microbiological tests relate not only to the specific plant, but also to specific locations within the plant, an adequate amount of baseline data on the microbiological characteristics of the sampling site is accumulated before model input values are developed and the data used for predictive purposes. The frequency at which these data are obtained determines whether trending information is used as part of defining input values. The more locations sampled, the greater the degree of differentiation between locations, and the greater the ability of the model to discriminate the susceptibility to MIC between various segments of the system. Consequently, plant engineers determine the level of sophistication desired to identify the susceptibility to MIC or the potential degree of severity of MIC at various locations within the plant.

The microbiological viability data are obtained via swab samples taken from the component surface of interest. When sites are not available for swab sampling, test surfaces of strategically located biofouling monitoring devices are used. Bulk water samples are of little use because bacteria that have colonized on surfaces, rather than those existing in bulk water, cause MIC. Data on water treatment chemicals and on the chemical characteristics of the bulk water are of little interest because they do not indicate the nature of the microenvironment within the microbiological colonies at the sites where potential corrosion can occur. The L/S MIC Index is expressed in Equation (30):

$$MIC\ Index = (BF) + (DFF) + (SF) \times (MF) \quad (30)$$

Where:

Microbiological Factor (BF) is the sum of input values for each of four types of microorganisms; ranges from 0 (not present) to 5 (highly viable)

Deposit/Fouling Factor (DFF) is the input value for deposits/bio fouling, measured by weight or visually; ranges from 0 (not present) to 5 (large amount of deposit/bio fouling)

Sedimentation Factor (SF) is the input value based on the flow velocity of water carrying a given amount of suspended solids at stagnant, intermittent, or continuous flow conditions; ranges from 0 (stagnant flow), 1 (greater than 10 ft. (3 m)/sec.), 3 (between 4 and 10 ft. (1 and 3 m)/sec.), 5 (less than 4 ft. (1 m)/sec.)

Material factor (MF) is the input value based on the published MIC-related corrosion tables for standard materials of construction; base metal range from 1 (very resistant) to 7 (very susceptible); welds/crevice sites range from 1 (very resistant) to 9 (very susceptible)

The index values are:

- MIC Index > 150, MIC is highly likely or severe, if existing.
- MIC Index > 75 but < 150, MIC concern is moderate.
- MIC Index < 75, MIC potential of the existing condition is low.

Section 7: Corrosion Inhibition

Corrosion inhibitors have been used successfully in the oil and gas industry for several decades for both sweet (CO₂) and sour (H₂S) conditions. A number of factors are considered in the choice of an effective corrosion inhibitor for protecting a steel surface. This section reviews the common primary issues considered when selecting a corrosion inhibitor product for an oil and/or gas production application. This is a guideline based on industry experience and as such makes suggestions that are generally considered to be good practice. As with any technical discipline, there are often examples found which contradict the general guidance.

Table 6
Comparison of Corrosion Resistant Alloy and Carbon Steel with Inhibition as Corrosion Control Design Options

Corrosion Resistant Alloy		Carbon Steel + Inhibition	
Advantage	Disadvantage	Advantage	Disadvantage
Low Opex	High Capex	Low Capex	High Opex
A good option for short pipelines or piping runs	Cost excessive for high pipeline length	No extra inhibition cost for long pipelines	Costly for short pipe runs, e.g. between compressors.
Minimal Inspection & Monitoring	Operational window (fluids, temperature) is fixed at design.	Regular Inspection and Monitoring	Typically a change of conditions is associated to a change of inhibitor product.
Minimal maintenance for operations	Exotic materials exhibit exotic the failure mechanisms.		High risk if the uninhibited corrosion rates are very high

Corrosion Control Economics

When selecting a corrosion control strategy, the primary choice is usually between a corrosion resistant material, or carbon steel and inhibition. Both have their advantages and disadvantages that are outlined in Table 6.

Good engineers and design houses usually have an idea of which approach is most appropriate based on experience. However, this is translated into a preconceived opinion that results in a choice being made based on the last project that was built and which is not fully tested. The best whole life cost is addressed when, at an early stage, the choice of type of steel or corrosion inhibition is addressed. This decision is a challenge for many projects, which are capital expenditure constrained.

The rest of this section considers the carbon steel and inhibition approach in more detail.

Corrosion Inhibition Selection

The performance of a corrosion inhibitor is influenced by many factors; ideally all those factors are part of the product selection. Often, this is a sequential process that progressively narrows the options to one or two product choices. Continuous revision of the decisions ensures that assumptions or decisions made at previous stages are compliant. A revision of the process (and a restart) is usually done if a product fails at the final stages. Consequently, sufficient time is commonly planned to allow for this possibility, especially if the conditions are expected to be challenging. Some operators have addressed this issue by pre-qualifying inhibitors for specific applications and/or by working more closely with a single inhibitor vendor to develop inhibitors for a specific application.

The following section details the primary factors normally considered when choosing an inhibitor product. These dictate the inhibitor chemistry type(s), to ensure that the product is transported to all of the metal surfaces requiring inhibition, and gets there at the appropriate dosage.

Water Composition

This includes the salt composition as well as the concentration of corrosive species (CO_2 , H_2S , organic acids and oxygen). The presence of salts generally increases the conductivity of the brine and hence makes the water more corrosive. The corrosiveness is reduced because of the presence of certain scale forming ions, such as bicarbonate, that reduce the formation of semi-protective films.

The water composition determines whether a given inhibitor is soluble, dispersible, or insoluble in a given brine. In extreme cases, small changes in water chemistry result in a transition between all of these states. Other ions, such as calcium, sometimes react with inhibitors to form insoluble salts, thus reducing or even eliminating any inhibiting properties.

Oil Composition and Water/Oil Ratio

For gas-only systems, this is not generally applicable and products are chosen that do not dry out and deposit "gunk" in the system. A completely covered metal surface ensures that the inhibitor is properly distributed. For pipelines, the technology includes the use of pigs or spheres that distribute the product around the full circumference.

When liquid hydrocarbons are present, it is important to distinguish between light (condensate) and heavier (crude) oils; the inhibitor solubility is likely to vary depending on the type of liquid hydrocarbon present. This, combined with the solubility in the water phase, determines how the inhibitor partitions between the water and hydrocarbon phases. The partitioning characteristic, together with the water to oil ratio (water cut), determine the actual concentration in the oil and water phases. Many commercial products are mixtures of different chemicals and each component has its own partitioning coefficient.

Presence of Solids

Generally, the presence of solids reduces the effectiveness of corrosion inhibitors, and for this reason it is good practice to keep equipment solids-free wherever possible. The adverse effects of solids result from:

- Adsorption of the inhibitor onto the solids, thus reducing the effective concentration of the inhibitor.
- Deposition of the solids in equipment that creates a physical barrier and stops the inhibitor from reaching the metal surface.

Erosion of the inhibitor film. This is primarily a concern for inhibitors applied using a batching technique since, once they are removed, the protection is lost until the next treatment.

Temperature

This applies to the range of ambient temperatures of the geographical location of the application and the operating temperature of the system.

Ambient Temperature: Product stability at the lowest and highest temperatures encountered is common. Sometimes the difference is high (e.g., a product manufactured in Houston that is transported by railcar and truck across the USA with a final destination in Alaska). A more cost effective solution is the use of different products for the summer and winter months when expensive solvents are used for cold temperature applications (e.g., in applications in Alaska, USA).

Operating temperature: Generally, it is the highest temperature that is considered, and sometimes it is located at specific equipment locations (e.g., compression, heat exchangers).

Velocity

The effect of velocity on corrosion inhibition was studied extensively during the 1990s following some high-profile failures. It was shown that the performance of some chemistries decreased as the velocity of the fluids increased. Today, products are available which perform at very high velocities ($> 20 \text{ m/s}$).

Initial Product Selection

One of the primary criteria for selecting a chemical as corrosion inhibitor is its efficiency to control corrosion. Several laboratory methodologies are available for determining the efficiency of corrosion inhibitors.⁸²⁻⁹¹

In order to select appropriate corrosion inhibitor it is not only important to use appropriate laboratory methodology, but also to use them under appropriate conditions. The influence of all parameters that would affect corrosion rate in the field should be simulated in the laboratory. They include compositions of steel, aqueous phase, oil phase, and gas phase (especially partial pressures of H_2S and CO_2), temperature, pressure, and flow.

Once the parameters above have been considered, it is possible to identify which inhibitor product types are the most appropriate and answer the following questions:

- Batch vs. continuous application
- Oil vs. water: soluble or dispersible
- Application Method (direct injection, capillary string, gas lift)

Once these questions have been answered and the potential products identified, the following criteria are typically considered.

Inhibitor Concentration or Batch Frequency

Optimal dosage and frequency to achieve the target corrosion rate. Initially, laboratory testing provides an indication. Ultimately, the optimum value is determined in the field.

Compatibility with Other Chemicals in the System

If other chemicals, such as scale, wax, hydrate, asphaltene, or bacterial inhibitors, are to be used, the compatibility of the entire cocktail is evaluated for stability and performance. The majority of chemical suppliers have products that are known to be compatible. However, if the products are supplied by different companies or if new products are developed, compatibility issues sometimes arise. For systems using multiple chemicals, it is common to identify a hierarchy of importance, usually based on the application, e.g., a hydrate inhibitor is identified first and compatibility with other products is investigated.

Environmental Characteristics

Traditional corrosion inhibitor chemistries based on amines and quaternary ammonium ions are harmful to the environment. During the last 10 years, significant progress has been made in the development of less harmful products.

Final Product Selection

At this stage, all of the data is evaluated and compared. In many cases, options are available which balance factors such as performance, cost and environmental considerations.

Inhibitor System Models: Efficiency vs. Availability

Once the inhibitor selection process has been completed, the performance is quantified in some way. For new developments, this is to determine the corrosion allowance (CA) to be applied. Historically, this was done using the concept of efficiency, but in recent years, a new approach based on availability has been developed. This section considers the two approaches:

Efficiency Model

In this model, a corrosion inhibitor product is assigned a performance efficiency (E%) that is defined as in Equation (31):

$$E(\%) = \frac{CR_u - CR_i}{CR_u} \times 100 \quad (31)$$

Where:

CR_u is the actual or predicted uninhibited corrosion rate.

CR_i is the inhibited corrosion rate

The uninhibited corrosion rate CR_u , is corrosion rate that occurs in the system when the inhibitor is not providing protection. The uninhibited corrosion rate is determined from a combination of:

- Corrosion modeling (see the discussion on corrosion models in the section of this document covering "systems containing only CO_2 " and "Important factors for corrosion prediction"). None of the CO_2 and CO_2+H_2S corrosion models predicts the effect of corrosion inhibition, only the uninhibited corrosion rate.
- Laboratory test data. Laboratory test data are used to assess uninhibited corrosion rates where conditions are outside of the application limits of the model(s).
- Field data on uninhibited corrosion rates. This is not as common as it is unusual; to operate corrosive systems without inhibitor for extended periods. It is possible to calculate a value for the uninhibited corrosion rate if values for the inhibited corrosion rate, the inhibitor system availability, and inspection data on the pipeline are determined.

The inhibited corrosion rate, CR_i , is the corrosion rate that occurs in the system when the inhibitor is providing protection. Based on laboratory and field data, some operators use the values below for inhibited corrosion rate in new designs are shown in Table 7.⁹²⁻⁹⁴

These values are set as the targets for the inhibitor-testing program. If lower inhibited corrosion rates are identified in the inhibitor testing program, these lower values are used to optimize the corrosion allowance (if not already fixed for the project) and in later risk-based assessments. Detailed inhibitor testing is usually only carried out in the detailed design phase of the project (by which time the pipeline, piping, and vessels have already been ordered and the corrosion allowance is not normally changed).

Table 7
Inhibited Corrosion Rates

Temperature Range, °C (°F)	Inhibited Corrosion Rate, CR _i , mm/y
Up to 120 °C (248 °F)	0.1
> 120 °C (248 °F) and ≤ 150 °C (302 °F)	0.2
Above 150 °C (302 °F)	Inhibition not done without specific testing

Once the facilities are in operation, the inhibitor system has been demonstrated as operational, and there is good feedback from the inspection and monitoring equipment, it is possible to re-assess the value of CR_i based on field data. From field experience, below 70 °C (158 °F), inhibited corrosion rates of < 0.05 mm/y are achieved. However, rates this low are not accurately measurable in the laboratory with the limitations of equipment and short term testing used for inhibitor selection, so are not used as a target for inhibitor selection.

For many applications, especially new developments, the efficiency is typically determined in the laboratory by measuring both CR_i and CR_u.

Once the efficiency is known, the corrosion allowance is calculated as shown in Equation (32):

$$CA = CR_u \times E(\%) \times \text{Lifetime of project} \quad (32)$$

The advantage of this approach is that it is simple to apply and everyone is familiar with the concept of efficiency. However, there are several disadvantages:

- Once an inhibitor is assigned, the same efficiency is used for all applications. Testing under all conditions is usually performed.
- Laboratory conditions are carefully controlled and very sensitive measurement techniques are normally used. The use of sensitive techniques sometimes indicates extremely low, inhibited corrosion rates that yield very high efficiencies. In practice, such low corrosion rates are not achievable in the field.
- A corrosion inhibitor is used to reduce the corrosion rate to that used for the design of the facility. This focus is often lost when discussing efficiency. A high efficiency does not always ensure that the design corrosion rate is met.
- It assumes that throughout the life of the operation, the availability of the inhibitor is 100%, where the availability is defined as the fraction (f) or percentage (A%) of time that the inhibitor is applied at the correct dosage. In many cases, this has proven to be the weakest link for a corrosion inhibitor application. Delivery issues pump problems, and poor communications regularly cause the inhibitor to either be switched off or not at the expected dosage.

For these reasons, several operators have moved to a different model of inhibitor performance known as the Availability Model.

The availability model addresses the deficiencies of the efficiency model by using Equation (33) to determine the corrosion allowance:

$$CA = (A \times CR_i + (1 - A) \times CR_u) \times DL \quad (33)$$

Where:

CA, CR_i, and CR_u have the meanings defined previously

A is the availability fraction defined as the fraction of time the inhibitor system is working correctly

DL is the design life of the equipment.

This equation is simplified if the target corrosion rate, CR_i is defined. If the design rate of CR_i is 0.1 mm/y, then it becomes Equation (34):

$$CA = (0.1A \times CR_i + (1 - A) \times CR_u) \times DL \quad (34)$$

Table 8
Examples of criteria for Inhibitor System Design to Meet a Specified System Availability

Item	A = 0.95	A = 0.99	A > 0.99
Inhibitor demonstrated as suitable for the application	✓	✓	✓
Inhibitor injection pumps	Standard	High reliability	High reliability
Back up pumps	✗	✓	✓
Check that pump is operating	Daily manual check	Automated alarm	Automated alarm
Pump planned maintenance	Annual	Annual	Usually more often
Inhibitor tank levels	Daily manual check	Automated alarm	Automated alarm
Report on inhibitor used (or report on compliance with key performance indicators) to responsible corrosion engineer	Monthly	Weekly	Daily
Quarterly manual check on pump injection rate	✓	✓	✓
No flow alarm (zero differential pressure across a critical component, or in line flow meters)	✗	✓	✓
Liquid samples for analysis of residual inhibitor levels and water chemistry	Monthly	Monthly	Usually more often
Corrosion monitoring system response time.	Response time such that total number of events x time to respond is < 18 days	Response time such that total number of events x time to respond is < 4 days	Response time is less than inhibitor persistency
Typical choices for corrosion monitoring equipment and system response times	Annual manual corrosion measurements	On line ER probes; response time 1-4 days and daily inhibitor injection concentration	On line fast response monitoring systems; response time 1-24 hrs and 6 hourly inhibitor injection concentration
Comprehensive review of uninhibited events	Desirable	Desirable	Desirable
Persistency taken into account	✗	✗	✓
Allowed days of uninhibited events per year (inhibitor system downtime, taking account of the persistency)	18	4	0-4
Shut in if inhibition system goes down for greater than a defined period of time	Rarely an issue	Possibly	✓
Check for worst case corrosion in shutdown conditions	Rarely an issue	Possibly	✓
Identify Operations Technician with responsibility for the inhibition injection system	✓	✓	✓
Corrosion Engineering Involvement	Monthly review	Weekly review	Daily review
Key Performance Indicators set for Operations Technicians and Corrosion Engineers	✓	✓	✓

Note that this initial simplified approach takes no account of persistency and it assumes production continues during uninhibited events. Inhibitor distribution after an uninhibited event is not considered and the details of individual uninhibited events are not considered. For high temperature and/or highly corrosive systems, these areas are usually addressed in more detail. In high corrosion environments and/or for a long design life, it is common to design for a very high availability ($A > 0.99$).

For a system in operation, the actual and worst case predicted future inhibitor availability is determined respectively from historical data and from a review of uninhibited events. In operations, the actual inhibited corrosion rate is measured. These data are used to determine the actual overall corrosion rate that is used in risk-based inspection assessment.

In assessing uninhibited events, the inhibitor persistency is taken into account (i.e., the period of time that the inhibitor continues to work for, after the inhibitor injection has stopped). In the design phase, this is used to assess equipment availability and repair times. For example, if the inhibitor persistency was 12 h, the design could ask that all inhibitor pump breakdowns be repairable in 12 h, so that a pump breakdown would not lead to an uninhibited event.

Care is taken in deciding how accurately persistency determined in the laboratory reflects on what happens in the field; the laboratory determined persistency is usually de-rated to account for this unknown factor. The persistency is accurately determined in the field, once the system is in operation. Then only uninhibited events which are longer than the persistency period are commonly considered when assessing the availability. Guidelines are usually put in place for how long it takes to re-coat the pipeline with inhibitor after the persistency period has been used (i.e., the inhibitor film has broken down because the uninhibited event is longer than the inhibitor persistency).

Selecting the Appropriate Inhibitor System Availability

The initial starting point for A is typically 0.95 (95 %). This value of A equates to 18 days inhibitor system downtime per year. This is typically achievable with a basic inhibition system (as illustrated below).

Using the same basic inhibition system, the value of A is usually reduced if there are known specific operating difficulties in the location the pipeline is installed (e.g. limited access, maintenance problems, taking account of comparable performance on existing systems etc.). This is typically assessed in the preconceptual design and conceptual design phase.

The value of A used in the design is increased with the use of more automated systems, faster response monitoring, back-up systems, etc. Examples of systems that meet typical criteria for inhibitor system availability are shown in Table 8.

The choice between the inhibitor systems selected has to consider a number of factors:

- For a particular operating location, the more sophisticated equipment used for high availabilities is sometimes difficult to procure initially, and it is potentially more difficult to get spare parts for maintenance
- Staffing levels vary by location; in some locations, it is typical to employ a large number of local staff, so automated systems are sometimes impractical. In other locations, the number of staff visiting a location has to be strictly limited (e.g., not normally manned platforms).
- Lower system corrosion allowance is usually linked to higher availability. An economic assessment of acceptable options is typical.

A large number of systems installed are of the basic type. Although an availability of 0.95 is achievable with this setup, availabilities as low as 0.50 have been assessed in actual field situations where the operations element has not been adequately addressed. Backup systems and automation are typically considered during the design to avoid such problems. The achievement of $A = 0.95$ is usually dependent on the people element, particularly during operation. This level of availability is not achieved unless there is adequate training and emphasis from management (e.g., key performance indicators to be met). If systems are designed in such a way that there is potentially a conflict between a focus on production and a focus on achieving availability, the inhibition system suffers.

For all of these systems in operation, once the system effectiveness has been demonstrated, it is sometimes possible to optimize the inhibitor system monitoring and control to one or two key performance indicators. In operation, the inhibited system availability are assessed on a regular basis and compiled annually as an input to the risk-based assessment of the system. The closer the availability is to 100%, the longer the inspection interval and the longer the life of the facility.

Section 8: Effect of Hydrocarbons

Modeling the effect of crude oil in CO_2 corrosion is not an easy task. Even though many researchers have worked in the area, the complexity of the chemical nature of crude oil makes it hard to generalize their behavior or to develop a mechanistic model. Most, if not all, of the work that has been done in the area is either experimental or based on field data. Even though there is plenty of work to be done, there is at present a better understanding of the effect of hydrocarbons and also of the relevance of including its effects into the available prediction models.

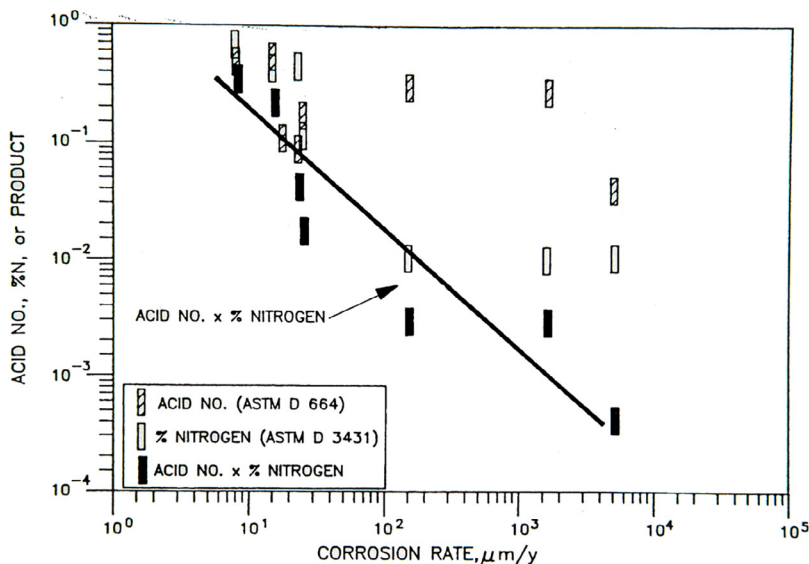


FIGURE 8: The Relationship of the Acid Content (Acid Number) and Organic Nitrogen Content of Crude Oil on Steel Corrosion Rate in Crude Oil/Brine Mixtures (4% NaCl Brine at 5.2 MPa CO₂ Pressure and 85 °C [185 °F])

pressure to the steel corrosion were extremely conservative, and very high corrosion rates were predicted by not accounting for the effect of crude oil.

As a first approximation, they related the effect to the protectiveness of the corrosion product layer formed on the steel, related in turn to the organic nitrogen and acid contents of the crude oil. Because of the similarity of the effect of crude oil and an amine based corrosion inhibitor on the corrosion rates of steel, the organic nitrogen content was considered as a possible indicator.

An empirical correlation was developed relating the product of acid number times the nitrogen content to the protectiveness offered by the crude oil (See Figure 8).

In 1991, Lotz et al performed a study with the aim of quantifying the extent to which hydrocarbons decrease corrosion with specific reference to hydrocarbon composition, classifying them on the basis of their kerogen type and maturity.¹⁰¹

From here on, both interfacial properties (to determine what wets the surface) and fluid dynamics (responsible of transporting liquids to the surface) were examined so no significant corrosion occurs when the hydrocarbon is the continuous phase.

In the case of hydrocarbon-in-water dispersions, the differences in degree of reduction of the corrosion rates were tentatively related with the maturity of the hydrocarbon as given by its density. Immature hydrocarbons dispersed in water tend to reduce corrosion rates more markedly than mature ones.

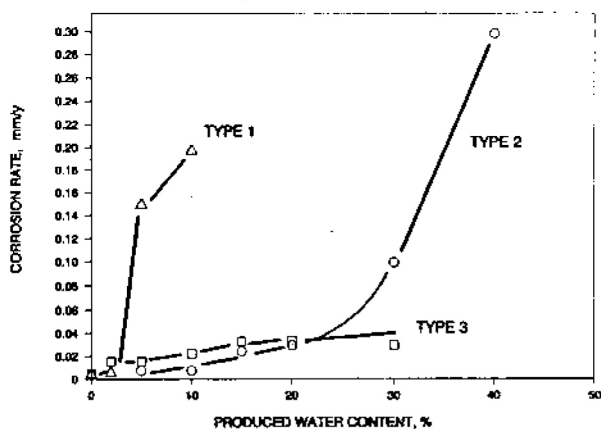


FIGURE 9: The Change of Corrosion Rate of Steel in Crude Oil/Produced Water Mixtures with Increasing Produced Water Content Showing the Three Types of Behavior Observed

This section briefly describes the effect of crude oil/hydrocarbons on CO₂ corrosion, a critical review of the current knowledge base and a brief description of the available models that include this effect.

Most authors agree that both wettability and changes in the brine chemistry are the major ways in which crude oil affects the corrosion of carbon steels in production environments. These two effects, in turn, are a consequence of the specific chemistry of the crude oil.

The study of polar constituents in crude oils and condensates have been pursued since the early 1950s, especially in the field of reservoir engineering.^{95,96} The characterization of polar constituents in crude oil extracts, as indicators of wettability properties in rock/oil/brine systems was studied in the 1970s and 1980s.⁹⁷⁻⁹⁹

The first attempts to model the effect of crude oil in corrosion were made by Efird and Jasinski in 1989.¹⁰⁰ They demonstrated that experimentally derived equations relating temperature and carbon dioxide partial pressure

to the steel corrosion were extremely conservative, and very high corrosion rates were predicted by not accounting for the effect of crude oil.

As a first approximation, they related the effect to the protectiveness of the corrosion product layer formed on the steel, related in turn to the organic nitrogen and acid contents of the crude oil. Because of the similarity of the effect of crude oil and an amine based corrosion inhibitor on the corrosion rates of steel, the organic nitrogen content was considered as a possible indicator.

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In the case of hydrocarbon-in-water dispersions, the differences in degree of reduction of the corrosion rates were tentatively related with the maturity of the hydrocarbon as given by its density. Immature hydrocarbons dispersed in water tend to reduce corrosion rates more markedly than mature ones.

Even when no actual modeling or prediction was made at this stage, the confirmation of both fluid dynamics and interfacial properties playing a role and the differentiation of behavior among crude oils with different origins played an important role in nourishing the knowledge base of the effect of crude oil.

Also in 1991, Efird stressed the importance of testing the effect of specific crude oils and including it in corrosion prediction and testing introducing the definition of corrosion rate break as the level of produced water in crude oil production where corrosion is accelerated and becomes a problem.¹⁰²

He found that the corrosion rate vs. produced water content curves for different crude oils commonly fall into one of three general types, as shown in Figure 9.

This shows that the onset of accelerated corrosion in crude oil production is difficult to predict by using a predetermined produced water level, and also explains how different crude oils show very different wettability properties and offer different degrees of protection.

In 1993, Smart¹⁰³ presented another piece of work, relating petrophysical data and wettability properties to corrosion. Based on the work by Anderson in 1986, Smart indicated that wettability is often strongly affected by surface active compound present in the crude oil. These surface active compounds are believed to be polar compounds containing oxygen, nitrogen or sulfur which are more prevalent in the heaviest fractions of crude oils such as resins and asphaltenes.

The polarity of the crude oil and of the corrosion products such as iron oxide, iron carbonate or iron sulfide are considered a major factor in wettability. The polarity of a crude oil is described as a synergistic action of its polar and polarizable molecules, such as resins and asphaltenes and its hetero/atomic compounds: nitrogen, sulfur and oxygen.

The presence of these polar constituents could change wettability as related to corrosion by reducing the interfacial tension between water and oil and by changing the tendency of crude oil to wet the surface.

In 1993, De Waard et al developed an empirical factor to be used in his widely known prediction correlation. His expression of corrosion rate is as shown in Equation (35):

$$\log(V_{corr}) = 5.8 - \frac{1710}{273 + t} + 0.67 \log(pCO_2) \quad (35)$$

A multiplier (F_{oil}) equal to one is added when water cuts are higher than 30% and flow velocities bigger than 1 m/s. These critical flow rate and water percentage come from the work done by Wicks et al¹⁰⁴ and Lotz et al,¹⁰⁵ respectively. When these conditions are not met, it is assumed that the steel is oil wetted and water is entrained in the crude oil, then the multiplier is zero, meaning no corrosion rate.

This multiplier was improved in 2001 to include different modes of water entrainment, linking API gravity to the water-in-oil emulsion stability which, in turn, is linked to the effect of oil wetting of the metal. At this point, the multiplier was written as shown in Equation (36):¹⁰⁶

$$F_{oil} = 0.545 \frac{\alpha}{90} + 4.3WU_{liq} \left(1 + \frac{\alpha}{90}\right) \quad (36)$$

Where W is the average water fraction of the liquid measured at the wellhead, U_{liq} is the liquid velocity in m/s, and α is the angle of deviation (in degrees) of the tubing from the vertical. This factor, however, comes from fitting observed field data with corrosion rates predicted with a semi-empirical model for CO_2 corrosion, and was exclusively developed for very light oils.

Equation (37) is expressed in three terms, that is, ($F_{oil} \leq 1$):

$$F_{oil} = 4.3WU_{liq} + 0.545 \frac{\alpha}{90} + 4.3WU_{liq} \frac{\alpha}{90} \quad (37)$$

It is suggested by De Waard et al. that the influence of light crude oils on corrosion rates in near liquid full systems consists of three contributions, so they tried to link each of these contributions to a specific mode of entrainment.¹⁰⁷

They defined three modes of water entrainment: mode I being water in oil emulsion, modes II and III when water separate from the crude oil phase. In mode II, conditions are such that the water phase remains stationary at certain locations (with oil flowing around it) while in mode III, water moves with the fluid, thus wetting the steel intermittently.

Based on the results from Craig¹⁰⁸ and using 10% water as an indicator of the emulsion breakpoint, they derived a relationship between the API gravity and the emulsion breakpoint ($50 > API > 20$) in Equation (38):

$$W_{break} = -0.0166 \times API + 0.83 \quad (38)$$

W_{break} is regarded as an indication of the interfacial tension between the crude oil and the water: the lower this tension, the higher the amount of water which is typically present as an emulsion in the oil. When the interfacial tension between oil and water is low, the interfacial tension between metal and oil is also lower, resulting in a better wetting of the steel by the oil, thereby reducing the rate of corrosion.

According to this, an oil factor was generated, which changes as the water cut changes in relation to W_{break} , as follows in Equations (39) to (42):

$$F_{oil} = 0.071 \frac{W}{W_{break}} U_{liq} \quad (39)$$

$$W < W_{break}, F_{oil} \leq 1 \quad (40)$$

$$F_{oil} = 0.071 \frac{W}{W_{break}} U_{liq} + 0.545 \frac{\alpha}{90} + 0.071 \frac{\alpha}{90} \frac{W}{W_{break}} U_{liq} \quad (41)$$

$$W \geq W_{break}, F_{oil} \leq 1 \quad (42)$$

At higher water cuts, the validity of Equation (36) becomes limited and does not obey the boundary condition that F_{oil} approaches 1 when the water cut approaches 100%. So, at high water cuts, an additional constraint is added to Equation (43):

$$F_{oil} \geq W \quad (43)$$

Also, for very low flow velocities or near-stagnant conditions, Equation (44):

$$U_{liq} < \frac{\alpha}{90}, F_{oil} = 1 \quad (44)$$

This approach links oil wetting properties with API gravity of the oil. However it does not consider the influence of crude oil properties which affect the stability of water in oil emulsions.

In this regard, the work presented by Hernández et al. in 2002 gave insight into the variables in crude oil composition that are potentially playing a major role in the inhibition offered by crude oils.¹⁰⁹ In this work, a statistical analysis was performed with several Venezuelan crude oils evaluated experimentally under the same conditions. The type of crude oil, either asphaltenic or paraffinic, and its concentration were found to be significant parameters when evaluating crude inhibiting effects.

For asphaltenic crude oils having more than 3% of asphaltenes in their composition, the most influential parameters at low crude oil concentrations were the sum of resins + asphaltenes and sulfur content. At high concentrations, the effect of sulfur content was not significant, and the sum of resins and asphaltenes dominated the inhibiting process.

In this case, the inhibiting capacity could be described by Equation (45):

$$\text{Inhibiting capacity (asphaltenic)} = 0.48 + 0.00444 \cdot (\% \text{crude oil}) + 0.00488 \cdot (\text{resins} + \text{asphaltenes}) + 0.0436 \cdot (S) \quad (45)$$

For those considered as paraffinic crude oils, having more than 50% of saturated components, the total nitrogen content, resins and asphaltenes were the variables found the most influential. At low concentrations, nitrogen was found to be the most significant parameter, indicating that the inhibition process is related to the adsorption of nitrogen-based compounds at low concentrations.

At higher oil concentrations, nitrogen content becomes less significant, and the inhibiting capacity is frequently related to the formation of stable emulsions because of the presence of polar functional groups found in the resin fraction.

The inhibiting capacity of paraffinic crude oils could be described by Equation (46):

$$\begin{aligned} \text{Inhibiting capacity (paraffinic)} &= 0.230 + 0.0026 \times (\% \text{crude oil}) + 0.0576 \times (\text{resins}) + 0.000844 \times (N) \\ &\quad - 0.333 \times (\text{asphaltenes}) \end{aligned} \quad (46)$$

When plotted, the results from this model look as shown in Figure 10.

The hypothesis of nitrogen compounds being responsible for providing inhibition in the aqueous phase was studied and published in 2003, when Hernández et al. identified organic compounds present in the aqueous extract of various crude oils and evaluated their adsorption capacities.¹¹⁰

The results showed here allowed the verification of the presence of higher amounts of compounds analogous to corrosion inhibitors in those fractions with higher adsorption properties. Nitrogen-based compounds, such as quinolines, tertiary amines, and anilines seemed to be closely related to both adsorption and corrosion inhibiting properties at low concentrations of crude oil. Carboxylic acids are also thought to be playing a role.

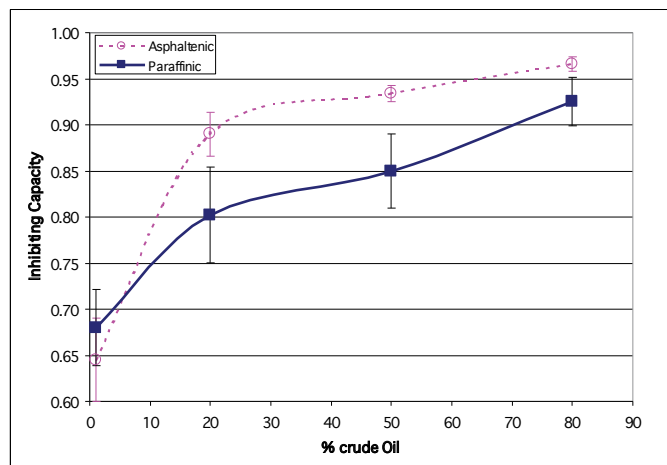


FIGURE 10: Variation of the Inhibiting Capacity with Crude Oil Content for Asphaltenic and Paraffinic Crude Oils

In 2004, Efird et al presented another conclusive paper evaluating seven different crude oils experimentally measuring two parameters:¹¹¹

- **Corrosion Rate Break:** This is used to determine the percentage of water in the crude oil where the corrosion rate increases dramatically. It's done with tests starting at 0% water and incrementally increasing the water content while measuring corrosion rates.
- **Equilibrated produced water corrosion rate:** defined as the corrosion rate in simulated produced water that is chemically equilibrated with the produced oil phase. The tests performed in this case are called brine corrosiveness tests and simulate the corrosion of steel in a separated water phase that is in equilibrium with the crude oil.

Corrosion rate break varies notably with the crude oil, meaning that each crude oil has different wettability properties, as expected from previous described works from Smart.

There was no apparent correlation between the corrosion rate break results and the corrosion rate reduction experienced by equilibrating the produced water with a crude oil. The reduction of corrosion rates in equilibrated produced water in comparison with only produced water occurs in many, but not all cases, showing that crude oil chemistry plays a major role in corrosion inhibition by crude oils.

As stated by Efird, crude oil affects CO₂ corrosion of steels in crude oil/water mixtures by either: changing the brine chemistry as a result of water soluble components of the crude oil or changing the wettability properties of the mixture. From here comes the conclusion of wettability preference and brine chemistry being two separate issues, in which crude oil chemistry plays a major role.

Both mechanisms are very hard to model, especially the first one. Wettability properties have been accounted for in several models already, as is seen in the next section. However, most wettability predictions are based on the density of the crude oil without taking into account many other properties of the crude oil that potentially affect its wettability properties.

Models Considering Hydrocarbon Effects

The IF model considers the effect of hydrocarbons based on three properties: oil-water emulsion, wettability, and the influence of oil phase of the corrosivity of the aqueous phase. Most models predict hydrocarbon effects based only on wettability. According to a review, the models considering crude oil wetting are: DW, LP, HY, PR, CP, MU, and EC. See Appendix B. The remaining packages included in this review, CA, KS, SP, SW, and OL, do not consider crude oil effects.

Section 9: Effect of Metallurgy

Carbon Steels: General Considerations

Oil and gas production industry continues to lean heavily on the extended use of carbon and low alloy steels, which are readily available and able to meet many of the mechanical, structural, fabrication, and cost specifications. From the materials cost point of view, the use of carbon and low alloy steel for tubing and pipelines is the most convenient option, and therefore, big efforts have been done in order to increase their corrosion resistance as well as their performance when the risk of sulfide stress cracking is present.

Metallurgical Alternatives for Carbon and Low Alloyed Oil Country Tubular Goods (OCTG) Products

According to API Specification 5CT, the various grades and groups of pipes furnished to this standard are made to a fine grain practice.¹¹² Steel made to a fine grain practice contains one or more grain refining elements such as aluminum, niobium, vanadium or titanium in amounts intended to result in the steel having a fine austenitic grain size. Seamless or electric-weld processes are acceptable depending on the specific product. Regarding chemical composition, the ranges of the main elements such as carbon, manganese, molybdenum, chromium and nickel are specified, depending on the product grade (Table 11). Heat treatments such as normalized and tempering or quenched and tempered are also specified to fulfill the parameters of each grade and group (Table 12).

In addition to those general specifications, pipe manufacturers have developed proprietary grades for certain particular applications (i.e., high mechanical properties plus sulfide stress cracking resistance) or to get certain improvement in CO₂ corrosion.¹¹³⁻¹¹⁸ Carbon and low alloy steel's performance in CO₂ environments depends on their microstructure and chemical composition.¹¹⁹⁻¹⁴² There has been much research done on these issues, but in spite of this effort, contradictions persist between the different available data.

The final microstructure of carbon and low alloy carbon steel OCTGs is determined by its chemical composition and the thermo-mechanical treatments used during the production processes. Depending on those parameters, a ferrite-pearlite or tempered martensite structure is obtained; the grain size and precipitation composition, morphology and size are also determined. Although the design criteria are mainly focused on properties such as mechanical resistance and toughness, the corrosion resistance is also affected by microstructure and chemical composition. Additionally, these two variables are not independent; the same microstructure is obtained with different chemical compositions, and vice versa.

Both laboratory experiments and field experience have shown that the performance of carbon steels with apparently the same composition and microstructure can vary greatly.

Effect of Chemical Composition and Microstructure of Carbon and Low Alloyed Steels on CO₂ Corrosion Performance

The microstructure is considered to have an effect on how firmly the corrosion scale sticks to the surface. The adherence of the corrosion product film, and hence its protectiveness, has often been related to the presence of iron carbide and its morphology (laminar, globular, etc.). The carbide phase strengthens the film and anchors it to the steel substrate, the size and distribution of these carbides become very important.¹⁴³ On the other hand, the accumulation of carbides in the corrosion product has been seen as the cause of increasing corrosion rate over time of exposure for ferritic-pearlitic (F/P) steels.¹⁴⁴

At present, there is no general agreement about the mechanism through which microstructure affects the growth and stability of the iron carbonate film. It has been reported that plain normalized steel with a ferritic-pearlitic microstructure is far superior to the quenched and tempered alloy steel with a martensitic microstructure, and vice versa.

Stegmann et al studied the effects of temperature, chloride concentration, and metallurgy on flow induced localized corrosion. They proposed that the needle-like carbide structures provide a better anchoring surface for the FeCO₃ than large ferrite areas interdispersed by a few pearlite grains. However, when they compared two N80 grades with similar composition and different microstructure (F/P vs. martensite bainite) they did not find marked differences in the corrosion rates.

Ueda and Takabe also studied the effect of environmental factors and microstructure on the morphology of the corrosion products in CO₂ environments. They used two different steels: API 5CT J55 (F+P) and N80 (tempered martensite). Tests were performed in 5% NaCl, pH = 3.7, 0.3 MPa CO₂ and 80 °C (176 °F), during 96 h. Corrosion rates were evaluated by means of weight loss measurements. The authors found that N80 steel showed lower corrosion rates than steel API 5CT J55, but suffered localized corrosion. FeCO₃ was identified by x-ray analysis in the corrosion products for both steels. Inspection of the primary scale on API 5CT J55 showed the existence of lamellar cementite embedded in the film. The good localized-corrosion resistance of the API 5CT J55 steel was attributed to the presence of lamellar cementite. In the N80 steel, the cementite is homogeneously dispersed in the martensitic microstructure and because of the lack of anchoring, the corrosion products peel off partially.

Niece and Ueda pointed out the importance of steel microstructure and chromium alloying content from failure analysis of corroded well tubing steel grade L-80 employed for seawater injection service. They found marked differences in the corrosion resistance per-

formance for steels specified as API 5CT grade L-80 received from different steel manufacturers. They showed that the combination of a Q&T martensitic microstructure with chromium content within 0.5–1 wt % offered a better corrosion resistance than either this microstructural condition or the combination of a Q&T bainitic and martensitic microstructure with little or no chromium content (< 0.1%). They stated that the role of the microstructure in improving the steel corrosion resistance is not completely clear.

The positive effect of low Cr additions (up to 5%) on standard carbon steel in CO₂ corrosion is reported in the literature. It is proposed that chromium enriched surface films are formed and they cause a reduction of the corrosion rate.

Ikeda et al showed that the addition of low concentrations of Cr to steels decreases the corrosion rate. An analysis of the corrosion products was conducted and Cr enrichment was found. The authors reported that the corrosion products were also adhesive, stiff, and tough.

Niece et al studied the effect of both Cr addition (up to10%) and the microstructure on general and localized corrosion in production well environments. The corrosion rate observed for chromium steels was smaller than that of carbon steels. However, Cr bearing steel with an F/P microstructure presented a lower corrosion resistance than with a martensitic microstructure. The authors consider that the inhomogeneous F/P microstructure interferes in the formation of a homogeneous Cr-rich film on the steel surface. Furthermore, they analyzed the corrosion products by means of X-ray, EDX, and EPMA techniques. FeCO₃ was identified in almost all the corrosion products, and an enrichment of chromium content was observed by EDX analysis for the Cr bearing steels.

Niece et al also found as well that the minimum Cr content to reduce corrosion rates was a function of the test temperature. At 60 °C (140 °F), a beneficial effect was obtained when the Cr content was above 1%; at 80 °C (176 °F), a reduction in the corrosion rate was observed for Cr additions above 0.5% while 1% addition decreased the corrosion rate at 100 °C (212 °F).

Kermani et al showed that at 3% Cr or more, protective films form in conditions in which iron carbonate films are hardly stable and they typically grow at a pH as low as 5.

Corrosion Rate Prediction, the Effect Steel Microstructure, and Chemical Composition

The numerous models for predicting CO₂ corrosion consider the influence of different environmental variables, but the effect of steel microstructure and composition are considered in only a few of them.¹⁴⁵⁻¹⁵⁵ John et al used the type of AISI⁽⁶⁾ steel as an input variable in their corrosion rate calculations, whereas Gunaltun introduces a correlation to the chromium content.

The DW model is semi-empirical and based on experiments in a high-pressure test loop. The model combines a contribution of the flow-independent kinetics of the corrosion reaction with one from flow dependent mass transfer of dissolved CO₂. Steel composition and microstructure, CO₂ partial pressure, temperature, and pH are main variables.

The baseline corrosion rate is calculated considering the kinetics of the surface reaction and the mass transfer of the dissolved CO₂ from the bulk of the solution to the surface of the steel. It also takes the effect of steel Cr and C content (through compositional correction factors F_c and F_C) into account, which is indicated in Equation (47):

$$V_{cor} = \frac{F_{cr}}{\left(\frac{1}{V_r F_c} + \frac{1}{V_m} \right)}$$

(47)

Where:

V_r (surface reaction velocity, mm/y)
V_m (mass transfer velocity, mm/y) depending on the material's microstructure, as shown in Table 9.

Table 9
Material Microstructure Variables

Normalized Steel	Quenched and Tempered Steel
Surface reaction $\log(V_r) = 4.84 - \frac{1119}{T} + 0.58 \log(p_{CO_2}) - 0.34(pH_{act} - pH_{CO_2})$	Surface reaction $\log(V_r) = 5.07 - \frac{1119}{T} + 0.58 \log(p_{CO_2}) - 0.34(pH_{act} - pH_{CO_2})$
Mass transfer $V_m = 2.8 \frac{U^{0.8}}{d^{0.2}} P_{CO_2}$	Mass transfer $V_m = 2.7 \frac{U^{0.8}}{d^{0.2}} P_{CO_2}$

⁽⁶⁾American Iron and Steel Institute (AISI), 1140 Connecticut Ave., NW, Suite 705, Washington, DC, 20036.

Where:

$$p\text{HCO}_2 = 3.82 + 0.00384 t - 0.5 \log(p\text{CO}_2) \quad (48)$$

pH_{act} = Actual pH of brine, predicted using Oddo-Thomson correlation as shown in Equation (49):

$$\text{pH}_{\text{act}} = \log\left(\frac{\text{HCO}_3^-}{p\text{CO}_2}\right) + 8.68 + 0.00405 \left(t \frac{9}{5} + 32\right) + 4.58 \cdot 10^{-7} \left(t \frac{9}{5} + 32\right)^2 - 3.07 \cdot 10^{-5} P \cdot 14.5 - 0.477 \left(\frac{\text{TDS}}{58500}\right)^{0.5} + 0.193 \left(\frac{\text{TDS}}{58500}\right) \quad (49)$$

Where:

TDS = "total dissolved solids", the sum of ion concentrations in mg/L

P = total pressure.

U = liquid velocity (m/s)

d = hydraulic diameter of the tube (m)

pCO₂ = CO₂ partial pressure (kPa)

t = temperature (°C)

T = temperature (°K)

Table 10
Compositional Correction Factors

Normalized Steel	Chromium Steel
$F_{Cr} = \frac{1}{1 + 2.3Cr\%}$	$F_{Cr} = \frac{1}{1 + 1.4Cr\%}$
$F_C = 1 + 4.5C\%$	$F_C = 1$

The compositional correction factors are dependent on microstructure, as shown in Table 10:

To obtain the predicted corrosion rate, baseline corrosion rates are multiplied by protection factors. Carbonate and oil protection factors are considered through Equations (50)–(52):

$$T_{scale} = \frac{2400}{6.7 + 0.44 \log p_{CO_2}} \quad (50)$$

$$\log F_{scale} = \frac{2400}{T} - 0.44 \log(p_{CO_2}) - 6.7 \quad (51)$$

$$F_{oil} = 0.059 \frac{W}{W_{break}} U + \frac{1.1 \cdot 10^{-4} \alpha}{W_{break}^2 90} + 0.059 \frac{W}{W_{break}} U \frac{\alpha}{90} \quad (52)$$

Where:

W = water cut, expressed as fraction (range 0-1)

U = liquid velocity (m/s)

α = angle of deviation of the tubing (°)

W_{break} = maximum fraction of water in oil, which is calculated as:

$$W_{break} = -0.0166 \text{ °API} + 0.83$$

API = gravity of oil in °API

F_{oil} expression is applied in the range 50 > °API > 20. Outside this range we use:

F_{oil} = 1 if °API equal to or higher than 50

F_{oil} = (20) if °API is lower than 20

Corrosion Resistant Alloys (CRA) General Considerations

Corrosion Resistant Alloys (CRA) have been defined as alloys whose mass-loss corrosion rate in produced fluids is at least an order of magnitude less than that of carbon or low-alloy steel, thus providing an alternative method to using inhibition for corrosion control.¹⁵⁷ This definition is ambiguous because corrosion rates in produced fluids, even that of carbon or low-alloy steel, is not a fixed quantity. Nevertheless, it is an operational definition that emphasizes the fact that CRAs generally have low uniform corrosion rates in CO₂, H₂S containing environments. An alternative definition is: CRAs are alloys that are not carbon or low-alloy steels, because the CRAs span a

Table 11
Chemical Compositions (wt %) API 5CT¹⁵⁶

Group	Grade	Type	C		Mn		Mo		Cr		Ni	Cu	P	S	Si
			min.	max.	min.	max.	min.	max.	min.	max.	max.	max.	max.	max.	max.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	H40	—	—	—	—	—	—	—	—	—	—	—	0.030	0.030	—
	J55	—	—	—	—	—	—	—	—	—	—	—	0.030	0.030	—
	K55	—	—	—	—	—	—	—	—	—	—	—	0.030	0.030	—
	N80	1	—	—	—	—	—	—	—	—	—	—	0.030	0.030	—
	N80	Q	—	—	—	—	—	—	—	—	—	—	0.030	0.030	—
2	M65	—	—	—	—	—	—	—	—	—	—	—	0.030	0.030	—
	L80	1	—	0.43 ^a	—	1.90	—	—	—	—	0.25	0.35	0.030	0.030	0.45
	L80	9Cr	—	0.15	0.30	0.60	0.90	1.10	8.00	10.0	0.50	0.25	0.020	0.010	1.00
	L80	13Cr	0.15	0.22	0.25	1.00	—	—	12.0	14.0	0.50	0.25	0.020	0.010	1.00
	C90	1	—	0.35	—	1.00	0.25 ^b	0.75	—	1.20	0.99	—	0.020	0.010	—
	C90	2	—	0.50	—	1.90	—	NL	—	NL	0.99	—	0.030	0.010	—
	C95	—	—	0.45 ^c	—	1.90	—	—	—	—	—	—	0.030	0.030	0.45
	T95	1	—	0.35	—	1.20	0.25 ^d	0.85	0.40	1.50	0.99	—	0.020	0.010	—
	T95	2	—	0.50	—	1.90	—	—	—	—	0.99	—	0.030	0.010	—
3	P110	^e	—	—	—	—	—	—	—	—	—	—	0.030 ^e	0.030 ^e	—
4	Q125	1	—	0.35	—	1.00	—	0.75	—	1.20	0.99	—	0.020	0.010	—
	Q125	2	—	0.35	—	1.00	—	NL	—	NL	0.99	—	0.020	0.020	—
	Q125	3	—	0.50	—	1.90	—	NL	—	NL	0.99	—	0.030	0.010	—
	Q125	4	—	0.50	—	1.90	—	NL	—	NL	0.99	—	0.030	0.020	—

^aThe carbon content for L80 may be increased up to 50 % maximum if the product is oil-quenched.

^bThe molybdenum content for Grade C90 Type 1 has no minimum tolerance if the wall thickness is less than 17.78 mm.

^cThe carbon content for C95 may be increased up to 0.55 % maximum if the product is oil-quenched.

^dThe molybdenum content for T95 Type 1 may be decreased to 0.15 % minimum if the wall thickness is less than 17.78 mm.

^eFor EW Grade P110 the phosphorous content shall be 0.020 % maximum and the sulfur content 0.010 % maximum.

NL = no limit. Elements shown shall be reported in product analysis.

wide range in composition. The objective of this section is to enable the user to understand the limits of application of CRAs in CO₂ and H₂S environments from the point of corrosion. Unlike carbon steel, CRAs sometimes suffer from either localized corrosion or environmentally assisted cracking, depending upon the H₂S concentration, temperature, etc. For the purposes of this report, environmentally assisted cracking is not considered, because this topic has been covered extensively by another NACE committee report.

Unlike the case of carbon steel, the information on the corrosion behavior of CRAs in CO₂–H₂S systems is sparse. This is partly because corrosion is generally not a major issue for the CRAs, and the focus has been on stress corrosion cracking/ sulfide stress cracking. The following sections provide a brief review of the published corrosion data on these materials.

Types of CRAs

CRAs, from the point of view of oil country usage, consist of various grades of stainless steels, nickel base alloys, and titanium alloys. Of the stainless steels, martensitic stainless steels (13Cr and 13Cr–Ni–Mo grades) are the most widely used, followed by the duplex stainless steels¹⁵⁸. Nominal compositions of some of the representative CRAs are shown in Table 14.

Field Experience

Romero and Palacios¹⁵⁹ report favorable corrosion performance of 13Cr components in gas condensate wells containing up to 20% CO₂ and 5 ppm H₂S. The NACE survey provides information on the distribution in the usage of various grades of CRAs and the types of environments in which they are used.

Corrosion Data on Stainless Steels

The corrosion rates in flowing CO₂ containing environments decrease with an increase in Cr and Mo content of the alloys. This is illustrated in Figure 10 for a number of martensitic stainless steels. It is seen that in flowing wet CO₂ environment, the corrosion rate of

carbon steels is quite high, whereas the 13%Cr martensitic stainless steels show a negligibly low corrosion rate.¹⁶⁰ Similar results were found by Kimura et al.¹⁶¹ The low corrosion rate is attributed to the formation of passive film under these conditions. Increasing the Mo content also results in lowering of corrosion rates in CO₂-H₂S systems (Figure 11). For a given temperature, Kimura et al. suggested a corrosion-composition index as shown on the right hand side of Equation (53) below:

$$C.R.(mm/y) + (C.R.)_0 - K \times (Cr + 0.2 Ni + 0.25Mo - 20C) \quad (53)$$

Table 12
Process of Manufacture and Heat Treatment API 5CT

Group	Grade	Type	Manufacturing process ^a	Heat treatment	Tempering temperature min. °C
1	2	3	4	5	6
1	H40	—	S or EW	None	—
	J55	—	S or EW	None ^b	—
	K55	—	S or EW	None ^b	—
	N80	1	S or EW	^c	—
	N80	Q	S or EW	Q&T	—
2	M65	—	S or EW	^d	—
	L80	1	S or EW	Q&T	566
	L80	9Cr	S	Q&T ^e	593
	L80	13Cr	S	Q&T ^e	593
	C90	1	S	Q&T	621
	C90	2	S	Q&T	621
	C95	—	S or EW	Q&T	538
	T95	1	S	Q&T	649
	T95	2	S	Q&T	649
3	P110	—	S or EW ^{g,f,g}	Q&T	—
4	Q125	1	S or EW 9	Q&T	—
	Q125	2	S or EW 9	Q&T	—
	Q125	3	S or EW 9	Q&T	—
	Q125	4	S or EW 9	Q&T	—

^aS = seamless process; EW = electric-welded process.

^bFull length normalized (N), normalized and tempered (N&T), or quenched and tempered (Q&T), at the manufacturer's option or as specified on the purchase agreement.

^cFull length normalized or normalized and tempered at the manufacturer's option.

^dAll pipe shall be full body heat-treated. Full length normalized (N), normalized and tempered (N&T), or quenched and tempered (Q&T), at the manufacturer's option or as specified on the purchase agreement.

^eType 9Cr and 13Cr may be air-quenched.

^fSpecial chemical requirements for electric-welded P110 casing are specified in Table C.5.

^gSpecial requirements unique to electric-welded P110 and Q125 are specified in A.5 (SR11).

Table 13
Corrosion Rate Parameters for 13 Cr Alloys

Alloy	K0	K1	N	ΔG
13Cr	1.44x10 ²	0.097	0.43	6.32
14Cr-1.5Ni-0.5Mo	2.04x10 ³	0.038	0.22	9.25
12.5Cr-5Ni-2Mo	3.11x10 ⁷	0.021	—	16.4

Where:

(C.R.)₀ is a baseline corrosion rate

K is a constant depending on the temperature

Cr, etc. are weight percent of various alloying elements.

Equation (53) is used with caution since it was developed for a limited range of alloys (essentially from 13 to 15% Cr). Miyata et al offer a different index, , for the corrosion rate as a function of alloy composition.¹⁶² Popperling et al also showed that lowering the carbon from 0.2 to 0.02% in a 13Cr stainless steel significantly lowered the corrosion rate in CO₂ solution.¹⁵⁷ Mo also had a beneficial effect. The corrosion rate for these alloys decreased with time, suggesting a slow build-up of passive film.

It is often seen that the low corrosion rates are maintained even at temperatures as high as 120 °C (248 °F). However, at the lower temperatures, there is a risk of sulfide stress cracking. NACE MR0175/ISO 15156 contains the application limitations of these alloys in sour service.⁴⁴

Tomoe and Tezuka found that the corrosion rate of 13Cr stainless steel at 180 °C increased from 0.4 mm/y at 2 atm partial pressure of CO₂ to about 2.1 mm/y at 8 atm of CO₂, thereafter remaining relatively independent of pressure.¹⁶³ The effect of CO₂ partial pressure and temperature on the corrosion rate of martensitic stainless steel is shown in Figure 12 (Kimura et al.). The lines demarcate the corrosion rate of about 0.125 mm/y, with data above and to the right of the lines indicating higher corrosion rates. Flow does not appear to have a significant effect on the corrosion rate of duplex stainless steel, except at high velocities (Figure 13).

Corrosion Data on High Alloy CRA

The highly alloyed materials typically show low corrosion rates in CO₂ only environments. Therefore, corrosion tests of these materials have focused on sour environments where localized corrosion is of concern. Tsujikawa et al evaluated the localized corrosion resistance of Ni-base alloys in NaCl-H₂S solutions under static conditions.¹⁶⁴ They found that there is a critical pitting temperature for localized corrosion in this environment and that this correlated reasonably well with critical pitting temperature in 6% FeCl₃ (ASTM G48 test).

Table 14
Representative Corrosion Resistant Alloys and their Nominal Chemical Compositions

Type	Alloy Name	UNS ⁽⁶⁾ No.	Composition, weight percent									
			Fe	Ni	Cr	Mo	W	Cu	Co	Ti	Cmax	Other
Martensitic		S41008	Bal.		13						0.08	
	M13Cr		Bal.	4	13	1					0.02	
	S13Cr		Bal.	5	13	2					0.01	
	15Cr		Bal.	6	15	2					0.03	
Duplex SS	22Cr	S31803	Bal.	5.5	22	3					0.03	N:0.2
	25Cr		Bal.	6.5	25	3					0.03	N:0.2
Austenitic SS		S31603	Bal.	12	17	2.5					0.03	
	27-7Mo	S31277	Bal.	27	22	7					0.02	0.35
Ni-base alloys		N08825	30	42	22	3		2				
		N09925	22	42	21.5	3		2		2.2	0.03	
		N08028	34	31	27	3		1				
		N06985	19.5	Bal.	22	7		2			0.015	
		N06255	Bal.	50	25	8	3	1.2			0.03	
		N10276	5	Bal.	15.5	16	4				0.02	

Furthermore, they showed that the pitting tests conducted in the NaCl-H₂S environment correlated well with tests conducted in a NaCl-potassium thiocyanate solution, the latter being easier to prepare. Denpo and Ogawa¹⁶⁵ showed that for a 22Cr-25Ni-4Mo stainless steel, the critical crevice corrosion temperature was greater than 200 °C (392 °F) for H₂S pressures ranging from 10-3 to 2 MPa in a 3% NaCl solution. Felton et al¹⁶⁶ tested a number of austenitic stainless steels and Ni-base alloys in 150 to 30,000 ppm chloride solution containing 30 psi H₂S and 101 psi CO₂. The results are shown in Table 13.

Evans et al evaluated the effect of commingling seawater with production water on localized corrosion of CRAs.¹⁶⁷ In this case, they also studied the effect of the combined presence of O₂ with CO₂ under static and flowing conditions at temperatures of 30 and 60 °C (86 and 140 °F). The test results are shown in Tables 15 and 16.

Table 15
Results of Crevice Corrosion Test of High Alloy CRAs in Sour Environment

Alloy	Environment	Localized corrosion
UNS N08825	150 ppm Cl, 30 psi H ₂ S, 101 psi CO ₂ , 2044 psi N ₂ , 150 °C	No
	30,000 ppm Cl, 30 psi H ₂ S, 101 psi CO ₂ , 2044 psi N ₂ , 150 °C	Yes
UNS N08028	150 ppm Cl, 30 psi H ₂ S, 101 psi CO ₂ , 2044 psi N ₂ , 150 °C	No
	30,000 ppm Cl, 30 psi H ₂ S, 101 psi CO ₂ , 2044 psi N ₂ , 150 °C	Yes
UNS N06985	150 ppm Cl, 30 psi H ₂ S, 101 psi CO ₂ , 2044 psi N ₂ , 150 °C	No
	30,000 ppm Cl, 30 psi H ₂ S, 101 psi CO ₂ , 2044 psi N ₂ , 150 °C	No
UNS N06625	150 ppm Cl, 30 psi H ₂ S, 101 psi CO ₂ , 2044 psi N ₂ , 150 °C	No
	30,000 ppm Cl, 30 psi H ₂ S, 101 psi CO ₂ , 2044 psi N ₂ , 150 °C	No

Predicting Corrosion of CRAs

Masamura et al have proposed an empirical model for predicting the corrosion of 13 Cr stainless steels in CO₂ containing environments.¹⁶⁸ The corrosion rate is described in Equation (54):

$$C.R.(mm/y) = K_0 \times ((K_1 \times C_{NaCl}) + 1) P_{CO_2}^n \exp\left(-\frac{\Delta G}{RT}\right) \quad (54)$$

Where the parameters in Equation 54 are listed below for the three different 13Cr alloys:

Table 16
Test Results under Static Conditions

Material	Depth of attack in 22 weeks (mm)			
	30°C		60°C	
	20 ppb O ₂	200 ppb O ₂	20 ppb O ₂	200 ppb O ₂
Electroless Nickel	0.4	1.5	0.1	<0.1
3% Cr low alloy steel	0.3	0.4	0.2	0.4
13%Cr-1	1 & 0.4	0.2 & 0.3	1 & 0.5	2 & 1.4
13%Cr-2	0.8 & 0.7	0.9 & 0.4	0.1 & 0.5	1.2 & 1.4
13%Cr alloy-1	0.4 & 0.4	0.2 & 0.1	0.2 & 0.3	0.1 & 0.1
13%Cr alloy-2	0.1 & 0.1	0.8 & 0.4	0.15 & 0.1	0.2 & 0.1
22%Cr duplex	0	0	0	0
25%Cr superduplex	0	0	0	0
17-4PH	0	0	0.4	0.3
UNS S31603	0	<0.01	0	~0.01
Notes: (1) Results relate to bore surfaces of specimens; crevice results summarized (2) Two values are given for the 13Cr materials; the first relates to attack on the pins, the second to attack on the boxes.				

A more general model for CO₂-H₂S corrosion has been developed by Anderko et al.^{169,170} In this model, the cathodic and anodic reaction kinetics are computed as well as the corrosion and repassivation potential to predict the occurrence of uniform and localized corrosion.

Section 10: Oxygen Corrosion

Introduction

Basic chemical properties of oxygen are found in any level one chemistry textbook or the internet. However, a few salient points are emphasized here. Discussing the effects of oxygen in oilfield systems usually includes discussions about acids, the presence of H₂S, and the pH of the system.

Key points are summarized as follows:

1. The electron removing powers of oxygen, sulfur, and acid increase as the aqueous phase becomes more acidic.
2. The electron removing power of oxygen increases as the concentration of oxygen increases—all other things being equal.¹⁷¹
3. The abilities of both oxygen and acid to react in an aqueous phase via convenient chemical pathways are exceptionally good. This means they react rapidly.
4. The ability of solid sulfur to remove electrons via a convenient chemical pathway is somewhat hindered because it is a solid. This solid has a low solubility in aqueous phases. It is generally accepted that solid sulfur is typically in "contact" with metal in order for corrosion to occur.¹⁷² The transport mechanism of a solid particle to the pipe surface is different than the transport of a species already dissolved in the aqueous phase. Specific complexities of sulfur corrosion are not well understood, but it has been empirically established that solid sulfur, in contact with steel, drastically increases the corroding circumstances, especially the pitting mechanisms.¹⁷³ Sulfur, completely dissolved into a hydrocarbon phase, increases general corrosion rates and promotes pitting under certain circumstances.

Table 17
Test Results under Flowing Conditions

Material	Depth of Attack in 22 weeks (mm)			
	30 °C		60 °C	
	20 ppb O ₂	200 ppb O ₂	20 ppb O ₂	200 ppb O ₂
Carbon Steel	0.1	0.1	0.25	0.254
Electroless Nickel	0.4	0.2	0.2	0.1
1%Cr Low Alloy Steel	0.05		0.2	0.1
3%Cr Low Alloy Steel	0.5	0.3	0.2	0.2
13%Cr- ¹	0.2 & 0.05	0.1 & 0.2	0.2 & 0.2	0.2 & 0.3
13% Cr alloy- ¹	0.4 & 0.4	0.2 & 0.3	0.5 & 0.35	0.4 & 0.15
22%Cr duplex	0	0	0	0
25%Cr superduplex	0	0	0	0
17-4PH	0.1	0	3.8	0.6
UNS N07718	0	0	0	0
UNS S31603	0	0	0	0
Galvanic Couples				
L80 Steel/25% Cr	0.1	0.12	0.145	0.254
L80 steel/UNS N07718	0.1	0.1	0.2	0.254
3% Cr/25% Cr	0.5	0.2	0.2	0.2
UNS N07718	0.8	0.4	0.2	0.2
Notes: 1. Results relate to bore surfaces of specimens; crevice results summarized in Table 4. 2. For galvanic coupled specimens, depth of attack relates to anodic element (carbon steel or 3% Cr steel). 3. Two values are given for the 13Cr materials; the first relates to attack on the pins, the second to attack on the boxes. 4. 1.5 mm at flow disturbance. 5. 0.4 mm at flow disturbance.				

- The presence of corrosion products containing iron in its +3 oxidation state (ferric species) could be an indication of oxygen ingress into the system. The observation of Fe^{3+} species in the corrosion product, however, can also result from exposure of the corrosion product to air that can occur during sampling and testing. To use the presence of Fe^{3+} as an indicator of oxygen ingress into the system, care is taken to minimize corrosion product contact with air during sample collection and testing.

Much of our modern infrastructure is made from steel components, and oxygen is a principal corrodent. Predicting corrosion mechanisms is an essential part of managing steel-based entities. The discussion is divided into two general categories as diagrammed below.

Predicting corrosion phenomenon in steel entities exposed to atmosphere or to liquids equilibrated with the oxygen in the atmosphere (Case #2) is a different science than predicting oxygen-enhanced corrosion in systems assumed to be oxygen free (Case #1).

Models that predict degradation on the inside of oilfield systems are usually based on a "no oxygen" assumption. Predictive models following this assumption focus on other corroding factors known to be present such as CO_2 , H_2S , organic acids, destructive flow factors, etc. Oxygen ingress introduces corrosion mechanisms not accounted for and often negate predictive validity.

The following discussions in Case #1 use the effects of oxygen on steel (ferrous metals) as a frame of reference. Oxygen's interaction with alloys is not addressed in Case #1.

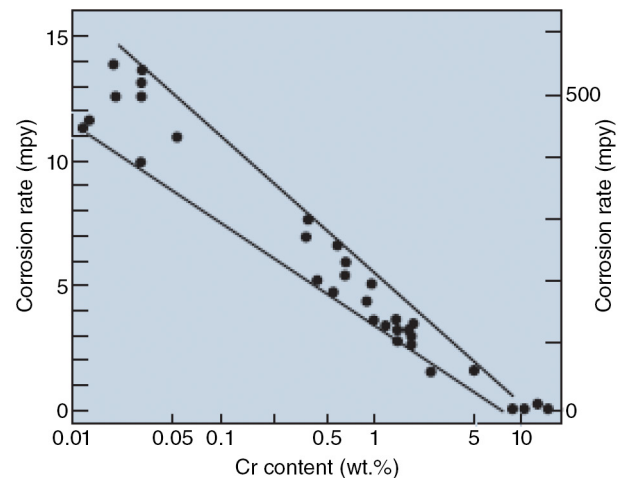
General Discussion on Oxygen Ingress

As discussed in the introduction, hydrocarbon producing and processing facilities are usually designed assuming no oxygen is present. However, oxygen (O_2) often gets into these systems and oxygen enhances corrosion rates above those expected without oxygen. Asset integrity is often managed using a risk-based approach that relies, in part, on the accuracy of predicting corrosion related failures. Oxygen ingress degrades the validity of most predictive models but often goes undetected until failures occur.

- Oxygen changes the corrosion mechanisms.
- Oxygen almost always enhances the corrosion process.
- Oxygen usually negates the validity of predictive models unless they were designed to include it.

Operators are generally reluctant to accept oxygen ingress as a possibility because they feel all measures have been taken to avoid this problem. Worse yet, it often goes misdiagnosed in the course of typical corrosion failure analyses. Field tests that detect and quantify oxygen ingress are used to convince related groups that this is the problem. Appropriate measures to find the source of ingress and fix the problem are initiated when test results show significant concentrations of oxygen in salient parts of the system.

Rigorous chemical explanations of oxygen-enhanced oil field corrosion are complex. However, it is appropriate to include a short treatise on this subject for practical use based on simple chemistry and field-based observations that highlight the following topics.



Effect of Cr content of commercial tubular goods on corrosion rate by loop tester

(Synthetic sea water, CO_2 partial pressure 0.1 MPa (60°C), test temperature 60°C, test duration 150h, flow velocity 2.5 m/s, specific volume: 800 cc/cm²)

FIGURE 11: Effect of Chromium Content of Alloy on Corrosion Rate in Wet CO_2

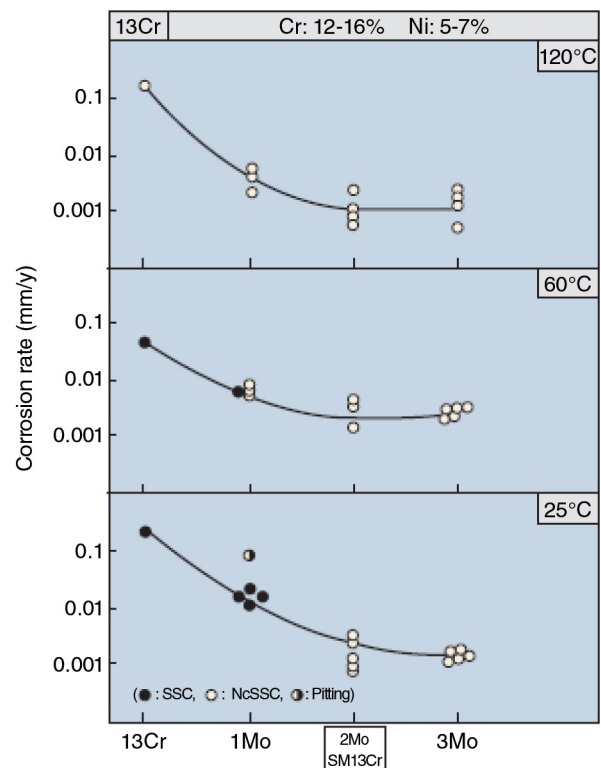


FIGURE 12: Effect of Mo Content of the SM13Cr Steel on Corrosion Rate in Wet CO_2

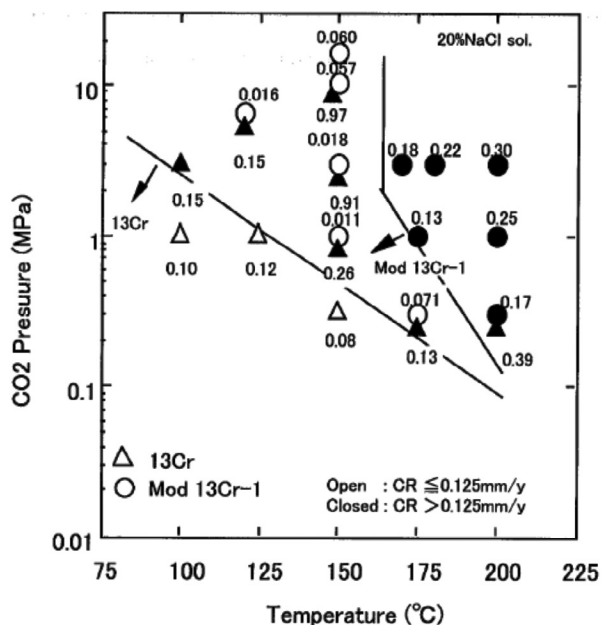


FIGURE 13: The effect of CO₂ Partial Pressure and Temperature on Corrosion Rate of 13Cr and 13Cr-1Mo Grades of Stainless Steels in Static Environments

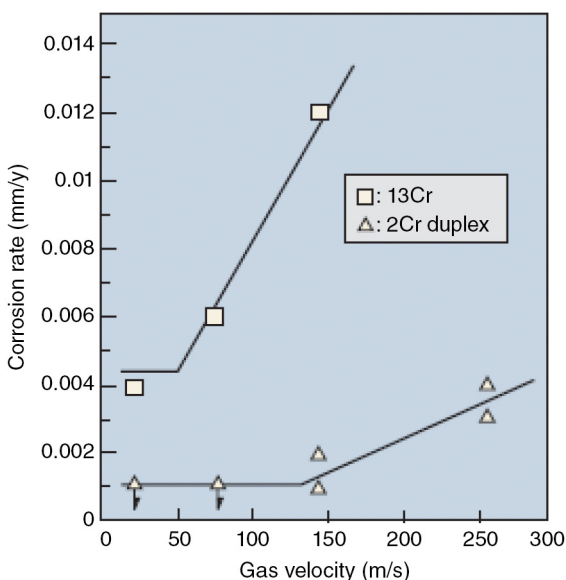


FIGURE 14: Effect of flow velocity on corrosion rates of two types of CRAs in wet CO₂

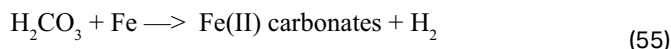
1. Consequences of oxygen ingress
2. Common ways that oxygen enters systems
3. The symptoms that reveal oxygen ingress
4. Methods of detecting and confirming oxygen ingress
5. Treating problems caused by oxygen ingress

Consequences of Oxygen Ingress–Sweet Systems

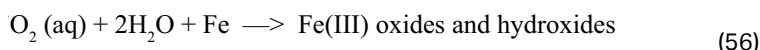
CO₂ dissolves into water to form carbonic acid which removes electrons from the iron and causes corrosion. This chemical reaction yields iron carbonate as the by-product. The iron carbonate forms scale on the steel surface which usually inhibits the corrosion reaction. The steel is said to be passivated when it is coated with iron carbonate.

Oxygen adds another chemical species that removes electrons from iron. This increases the overall corrosion rate and iron oxides formed from that reaction interfere with the formation of the iron carbonate passivating layer. Overall corrosion rates increase and pitting is encouraged.

Two efficient electron removing reactions are now active, those associated with dissolved CO₂ and those associated with O₂. Effective passivation of the steel is hindered by the presence of iron oxide. Carbonic acid driven corrosion mechanisms typically remove two electrons from each iron atom and the resulting by-products from that reaction are based on the Fe⁺² ion—symbolized as Fe(II), as shown below in Equation (55):



Siderite, FeCO₃, and hydrated forms of siderite (often called iron carbonate hydroxide, Fe₂(OH)₂CO₃) are typical markers of this process and are well characterized by X-ray diffraction (XRD). Oxygen usually removes three electrons from each iron atom and the resulting by-products from that reaction are based on the Fe⁺³ ion - symbolized as Fe(III), as shown below in Equation (56):



Corrosion by-products from carbonic acid become contaminated with iron oxide type scale where iron is in the +3 oxidation state.⁽⁷⁾ The following chemical species are often identified under these circumstances and are also well-characterized by XRD:

- Fe₂O₃-Hematite
- FeO(OH)-Goethite

Consequently, the protective scale associated with siderite (iron (II) carbonate) is disrupted enough to prevent uniform protection. Localized types of corrosion are enhanced when oxygen is present.

Most oil field chemical inhibitors are not designed to work in the presence of oxygen. The best inhibitors for specific sweet systems are usually selected using lab tests that exclude oxygen in the test sequence. Oxygen-tolerant corrosion inhibitors are rarely called for because of the “no oxygen” assumption. Mitigated corrosion rates based on lab studies and field monitoring do not apply when oxygen gets involved.

Oxygen generally causes or creates crevice corrosion. This has been well documented and studied.¹⁷⁴ Threaded fittings provide convenient crevices and are susceptible to this phenomenon. A method of detecting the presence of oxygen is to install coupons wound

⁽⁷⁾Magnetite Fe₃O₄ is an exception.

with monofilament type fishing line into a system close to where oxygen is suspected. Corrosion under the fishing line is related to the presence of oxygen. Crevices are not always present in a system, but the effects described above are still active.

Consequences of Oxygen Ingress: Sour Systems

When oxygen enters a sour system, problems multiply and persist. The possible chemical reactions are both numerous and complex. Based on observations, we know oxygen reacts with H_2S under many oilfield conditions to give elemental sulfur, S_8 , as summarized in Equation (57). The term “elemental sulfur” in this report refers to the most common form of sulfur (yellow solid). The sulfur atoms in this solid are combined into eight-membered rings, hence the chemical formula S_8 . The yellow solid is composed of these cyclic molecules that contain eight sulfur atoms. This reaction appears to take place in both the gas phase and the aqueous phase; high pressures enhance both the thermodynamic tendency of the reaction to happen and the chemical kinetics of the process, as shown below in Equation (57):



Sulfur is in the same chemical family as oxygen and has a similar tendency to remove electrons from steel. Sulfur occurs naturally in sour production and its presence is usually obvious. However, when sulfur suddenly shows up in selected parts of a sour system, chances are good there is oxygen ingress somewhere. If the pH of the system is above 7, the sulfur is converted to ionic polysulfides. Ionic polysulfides usually come from the formation but their sudden appearance commonly indicates oxygen ingress.

There are several points to make regarding sulfur:

- Sulfur is a solid composed of S_8 molecules and the particle size depends on how it is formed in the system.
- When sulfur is formed by oxygen ingress, the particle size is usually very small. These particles are easily transported by moving fluids.
- Sulfur is denser than oil or water (specific gravity is about 2 depending on the crystalline form) and normally falls to the bottom of a pipe in low flow situations.
- Sulfur is somewhat soluble in liquid hydrocarbons. This solubility is dependent on the chemical makeup of the hydrocarbon, the temperature and the pressure.
- Sulfur dissolved in hydrocarbons has been considered benign by the industry because it usually does not participate in aqueous-based corrosion mechanisms. Hence, oxygen ingress into sour systems is typically of lesser consequence if it reacts rapidly with the H_2S to form sulfur that promptly dissolves into a hydrocarbon phase. If the oxygen ingress occurs under a circumstance where this route is not active, the sulfur particles persist and become involved with the corrosion process. For example, if sulfur is formed in an aqueous phase that lies below an oil phase, it does not often dissolve because the two phases do not typically mix sufficiently.
- Sulfur particles typically enhance corrosion rates by an order of magnitude and promote an extremely aggressive pitting situation.
- Sulfur found in sour systems is usually mixed with several forms of iron sulfide such as mackinawite, pyrrhotite, and greigite. When this happens, the sulfur is not visually evident. Spot tests are used to detect sulfur in these samples, but XRD is the best way to confirm its presence.
- Corrosion tests have shown synergistic interactions with certain iron sulfides that result in aggressive pitting mechanisms.
- Sulfur is somewhat soluble in high pressure sour gas and the solubility is dependent on the concentration of H_2S in the gas, the temperature and the total pressure. This variable solubility provides additional complexities and another transport mechanism.
- Sulfur causes fouling and flow restrictions.
- When combined with pyrophoric iron sulfide, it often creates an extreme fire hazard when exposed to the atmosphere if allowed to dry out. Caution is used when disposing of solids removed from sour systems.
- Sulfur is often misdiagnosed as asphaltene when standard analytical methods are used to classify the composition of solids. This usually leads to incorrect conclusions about what is wrong with the system and how to treat the problems.
- The presence of ionic polysulfides is sometimes a marker of oxygen ingress into sour systems, depending on the pH of the aqueous phase. This topic exceeds the scope of this document.

Methods of Detecting Oxygen Ingress

Oxygen contamination is generally intermittent and is not easily detected. Experience has shown that a portable gas chromatograph is used as a sensitive real time monitor to detect the presence of oxygen in a gas phase. These chromatographs are connected to the gas line and set to sample the gas every 20 to 30 minutes. Case history #2 demonstrates the effectiveness of this approach. There are third party analytical labs that do this survey. The system is allowed to experience at least one complete cycle of its normal events while the chromatograph is connected.

Oxygen ingress into aqueous systems is constantly monitored using galvanic probes. These are available through companies that specialize in corrosion monitoring equipment. The advantage to this approach is constant monitoring that is capable of detecting intermittent oxygen ingress excursions. Galvanic probes are under-used in the upstream O&G production.

A chemistry-based method to measure dissolved oxygen is also used and is very accurate in aqueous environments

XRD Analyses of Solids Taken from a Corroding System

XRD analyses provide some of the best data to confirm oxygen ingress. As yet, there are no published correlations between precise thermodynamic conditions and the expected iron-oxygen species that are formed as a result of aerobic corrosion. However, useful guidelines have been developed based on a statistical review of the analytical results obtained from many dozens of samples of corrosion debris, recovered from systems where oxygen-mediated corrosion was either known or suspected. These guidelines are presented here.

There are three classes of Fe(III) compounds associated with corrosion because of oxygen ingress under O&G producing conditions.

- Species associated with Goethite-Iron (III) oxide/hydroxide (FeOOH)
- Species associated with Hematite-Hydrated Fe(III) oxides- $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$
- Species associated with Iron Hydroxide- $\text{Fe}(\text{OH})_3$

The least ambiguous markers for low temperature, oxygen-mediated corrosion are the iron oxide hydroxides (FeOOH). There are three types of iron oxide hydroxides; goethite (the most commonly observed in O&G samples), lepidocrocite, and akaganeite. All three of these species are described by the formula FeOOH and all three are readily identified by XRD. Of note is the fact that these compounds invariably form very broad, low-intensity peaks in the XRD scan, qualitatively different from the usually sharp Gaussian shape of geological and fully-crystalline materials.

Hematite (Fe_2O_3) and the more commonly observed magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) are sometimes indicators of oxygen ingress, but such an interpretation includes a wider assessment of context and the specific circumstances pertaining to that particular sample. The first thought when these compounds are identified is that they are components of mill scale that often remains on carbon steel surfaces as a by-product of manufacture (see discussion of mill scale, below). Factors that support the identification of hematite as a corrosion product are high abundance (greater than ten percent of the sample), knowledge that the failed component has been subjected to a high temperature environment (e.g., steam), and/or the absence of other mill scale components such as magnetite. Factors that support the identification of magnetite as a corrosion product are high abundance (greater than ten percent of the sample), and/or the presence of other significant corrosion markers in the sample (e.g., goethite).

There is a confusing factor in this topic, and that is mill scale. Mill scale is a thin layer or incrustation of iron oxides formed under the high temperatures used to fabricate pipe. Although mill scale is commonly cleaned out by the manufacturer before the pipe is sold for oilfield service, this cleaning function is sometimes done improperly, and consequently some of the remaining scale sloughs off (or is scraped off), and winds up in deposits sent for analyses.

Mill scale is typically composed of three compounds, one of which (magnetite) is very commonly observed in O&G samples of all types. Therefore, the corrosion specialist uses experience and context when finalizing the interpretation of XRD data. The three major components of mill scale, and some interpretive guidelines are given below:

1. Magnetite (Fe_3O_4) is a compound that contains both Fe(II) and Fe(III) ions in the crystal matrix. It has a distinct XRD reflection pattern and is readily formed at high temperatures during fabrication of the steel. It is also formed during the storage of pipe under surface conditions prior to installation in an O&G facility. For these reasons, the interpretation of magnetite in a corrosion-related sample is undertaken with some care. Typically, magnetite is not a marker of oxygen ingress. Factors that support the identification of magnetite as mill scale are low abundance (a few percent of the sample, or less), and/or the presence of other mill scale components such as wustite and hematite.
2. Wustite (FeO) is formed at high temperatures during the fabrication of steel. It is formed as a thin but very adherent layer closest to the steel surface. It has a distinct XRD reflection pattern; it is not a marker of oxygen ingress.
3. Hematite (Fe_2O_3) is formed as a minor constituent of mill scale. It is also formed as a corrosion by-product as a result of oxygen ingress under O&G producing conditions, usually in high temperature situations. Again, context is used to correctly interpret the XRD data, especially if hematite is the only marker present in the analysis. Factors that support the identification of hematite as mill scale are low abundance (a few percent of the sample, or less) and the presence of other mill scale components such as magnetite.

It is worth mentioning that XRD providers specializing in oilfield solids are preferred to other possible providers who let their computers select the best fit to the diffraction spectra. For example, goethite (common corrosion by-product found when oxygen enters produc-

ing systems) is occasionally misdiagnosed as ferrottychite, $\text{Na}_6\text{Fe}_2(\text{SO}_4)(\text{CO}_3)_4$, because the first three strong reflections in the XRD spectra are virtually coincident. This often happens when the XRD technician allows the computer to select the best fit from the associated mineral library. Ferrottychite contains iron in its +2 oxidation state and erroneous conclusions are drawn regarding the presence of oxygen. Ferrottychite is an uncommon mineral identified in plutonic formations such as the Khibiny Massif in the Kola Peninsula located in the Murmansk District of Russia, a highly unlikely compound to be formed by corrosion under oilfield conditions.

Predicting Corrosion Rates When Oxygen Ingresses into Systems Assumed to be Oxygen Free

Martin studied the effects of oxygen ingress into oilfield systems directly both in the field and in the lab using Linear Polarization Resistance (LPR) and gravimetric methods. This review is a good starting point if corrections for oxygen ingress are to be included into predictive models.

Martin concludes the following:

- Oxygen ingress enhances the corrosion rates in both sweet and sour systems.
- Dissolved oxygen predominantly affects the cathodic reaction.
- That oxygen is not preferentially reduced in systems containing CO_2 , H_2S or both, rather, the oxygen adds another oxidative (electron removing) mechanism that increases the corrosion rate above that caused by the acid gases.
- Dissolved oxygen seems to enhance the kinetics of the CO_2 corrosion mechanism in sweet systems.
- Dissolved oxygen in sour systems produces more complex phenomena that persist after the oxygen is eliminated.
- No mention of pitting corrosion is made, as most of his data was from LPR.

He offers several rules of thumb for predicting corrosion rates as a function of the concentration of dissolved oxygen resulting from air ingress. These rules-of-thumb are not given here because they are specific to the test conditions used and have to be applied as such. The reader has to decide if Martin's data is relevant to their specific circumstance.

Martin also reviews data where chemical inhibitors were used to mitigate corrosion when low levels of dissolved oxygen were present. This work clearly shows some inhibitor components are much more effective than others at mitigating corrosion when oxygen is a factor.

Oxygen Corrosion Prediction

Corrosion rates in oxygen containing environments are potentially predicted by an empirical equation developed by Pisigan and Singly as shown in Equation (58):¹⁷³

$$MPY = (TDS)^{0.253} \times (DO)^{0.82} \times (10 SI)^{0.876} \times (Day)^{0.373} \quad (58)$$

Where:

TDS: Total Dissolved Solids, mg/L

DO: Dissolved Oxygen, mg/L

SI: Langelier Scale Index

Day: Exposure Period, days

Oxygen in water obeys Henry's Law rather well; the solubility is roughly proportional to the partial pressure of oxygen in the air as shown in Equation (59):

$$pO_2 = KO_2 \times O_2 \quad (59)$$

Where:

pO_2 is the partial pressure of oxygen in torr,

xO_2 is the mole fraction of oxygen in oxygen saturated water,

KO_2 is the Henry's Law constant for oxygen in water (about 3.30×10^7 K/Torr for oxygen at 298 °K)¹⁷⁵

Many empirical equations are available to accurately estimate oxygen solubility as a function of temperature, pressure, and humidity. The more accuracy is required the more complex the equations are.

Equations (60) and (61) are two empirical equations that give the saturated dissolved O_2 concentration (DO) in mg O_2 /L water. They apply to oxygen in distilled water at a barometric pressure of P (in torr), at a temperature of t (°C), with a water vapor pressure of p (in torr):

Oxygen Related Corrosion Phenomenon that Impact Steel Entities

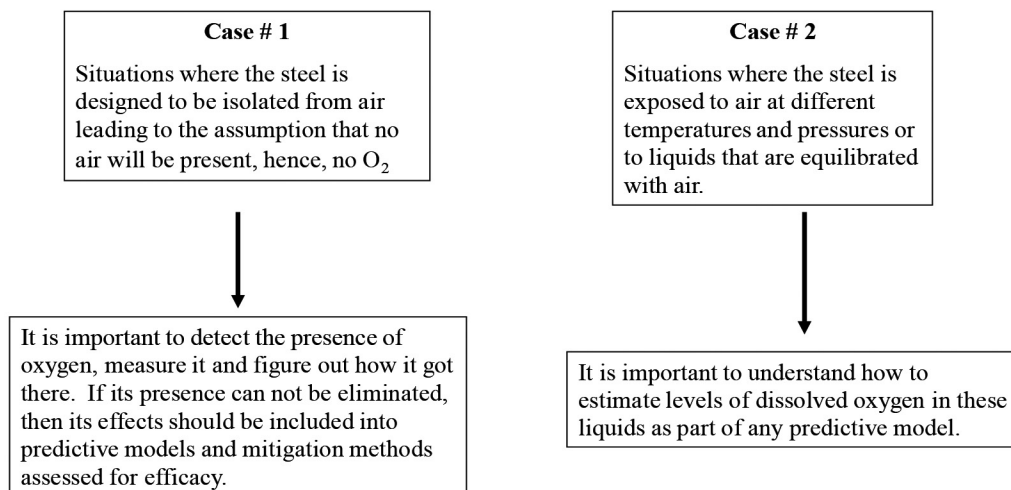


FIGURE 15: Oxygen Related Corrosion Phenomena that Impact Steel Entities

$$0\text{ }^{\circ}\text{C} < t < 30\text{ }^{\circ}\text{C}$$

$$DO = (P \cdot p) \times 0.678/35 + t \quad (60)$$

$$30\text{ }^{\circ}\text{C} < t < 50\text{ }^{\circ}\text{C}$$

$$DO = (P \cdot p) \times 0.827/49 + t \quad (61)$$

Calculations of dissolved oxygen in water is described in literature.¹⁷⁶

Duedall explained the behavior of oxygen in deep ocean. It was stated that oxygen solubility decreases with increasing temperature but increases with decreasing temperature.¹⁷⁷ The deep ocean gets its oxygen from water masses that form in northern and southern latitudes. These water masses, formed at the surface, sink because they are dense. Unlike nitrogen, however, oxygen is biologically active. Organisms consuming oxygen (respiration) cause oxygen concentration to decrease as the water mass moves away from its source. This is why we call oxygen a neoconservative gas: its concentration changes by biological processes in addition to mixing processes.

The solubility of oxygen is less than that of nitrogen; in other words nitrogen is more solubility in seawater than oxygen. At 25 °C (77 °F), the solubility of oxygen in seawater of 35 ppt is close to 4 mL per kg of seawater. At 0 °C (32 °F), the solubility increases to about 10 mL per kg of seawater. Cold water has more oxygen than warm water. The oceanographers currently use micromoles per kg as the units for oxygen rather than the older unit of mL per kg of seawater. Conversion of one unit to the other is accomplished using the gas law. Consider the case of 8 mL of oxygen gas per kg of seawater. What is the corresponding concentration in units of micromole of oxygen per kg? The gas law states that 1 mole of gas = 22.4 L of gas (22.4 L is about 22.4 average sized balloons). Thus, 1 mole = 22,400 mL. Therefore, 8 mL/kg x 1 mole/22,400 mL = 0.000357 mole/kg = 357 micromole/kg.

Oxygen (as a dissolved gas) is obviously important in the oceans owing to its role in biological processes. Photosynthesis produces dissolved oxygen (in the photic zone), and this process sometimes leads to oxygen concentrations that exceed its solubility. Some surface water, or water just below the surface layer, exceeds oxygen solubility by 10 to 20%. This is called super saturation.

Example of Oxygen Corrosion

Patton and references therein provided a good summary on oxygen corrosion cases. Effects of oxygen concentration and temperature on the corrosion of low-carbon steel pipes are indicated in Figure 15.¹⁷⁸

Conrad showed that of the three dissolved gases, CO₂, H₂S and O₂, oxygen is by far the most aggressive of the group.¹⁷⁹ If either or both of the other two gases are dissolved in the water, it drastically increases their corrosiveness. The higher the concentration of dissolved gases in solution, the higher the corrosion tendency.

Dissolved oxygen can cause severe corrosion at extremely low concentrations. Figure 16 shows measured corrosion rate as a function of dissolved oxygen concentration in Pacific Ocean water.¹⁸⁰

Oxygen Corrosion Morphology

Oxygen forms localized corrosion areas referred to as pits. This distinctive formation is readily distinguishable from acid attack, caustic gouging or chelate corrosion (See Figure 17). It is characterized by large shallow, flat bottomed pitting that removes large areas of surface metal (Figure 18). The edges of the pits gradually slope and run into other pitting, and the entire surface is usually covered with pits. Oxygen pits rapidly “drill” through metal surfaces, leading to metal fatigue and failure.

Section 11: Flow Enhanced Corrosion and Erosion Corrosion

Introduction

With a few exceptions, most metals and alloys owe their corrosion resistance to a protective surface film. Erosive fluids damage the protective film or remove surface material, leading to a significant increase in penetration rate. For example, carbon steel pipe carrying water is usually protected by a film of rust and its corrosion rate is typically < 1 mm/y (or 40 mils/y). The removal of this oxide film by an erosive slurry gives corrosion rates on the order of 10 mm/y (400 mils/y) in addition to any erosion of underlying metal.^{181,182} Damage to the protective film is sometimes the result of fluid-induced mechanical forces or flow-enhanced dissolution.^{183,184} Meanwhile, corrosion leads to degradation of surface properties and promotes mechanical erosion under action of the mechanical forces.¹⁸⁵ This conjoint action of erosion and corrosion is known as erosion corrosion. This section presents an overview of the subject matter from an R&D perspective and an engineering perspective. The former tends to cover the more fundamental aspects and the latter covers the more pragmatic concerns. The practicing engineer usually uses both approaches to make informed choices regarding the prediction and management of such mechanisms. A number of pertinent references and support reading material are presented to support the information presented in this report.

Typical Industry Problems

According to a recent survey, erosion corrosion was rated as one of the top 5 most prevalent forms of corrosion damage in oil and gas production and the cause of immense economic losses.^{186,187} Examples of typical problems of erosion corrosion in oil and gas systems are:

- Downhole components. Petroleum and mining drill bits are subjected to highly abrasive rock fragments and high velocity fluids so that erosion corrosion is among the most common failure mechanisms of downhole components.¹⁸⁸ During drilling operations the drill pipe and the internal surface of the casing are exposed to erosion.
- The entire downhole tubing string is sometimes exposed to erosion corrosion, although this is dependent upon the composition of the fluid being produced. Internal tubing walls are typically oil wetted, so they are not particularly subject to corrosion and therefore not subject to flow-accelerated corrosion (FAC) or erosion corrosion (although they are potentially susceptible to straightforward erosion), however Water-oil ratio, crude characteristics and other variables may conduce to a different outcome. Water dropout to allow corrosion (and FAC and erosion corrosion) of downhole tubing is dependent upon a wide range of factors – composition, temperature, API gravity, angle of deviation of the well, flow rates, flow regime, fluid phases, etc.

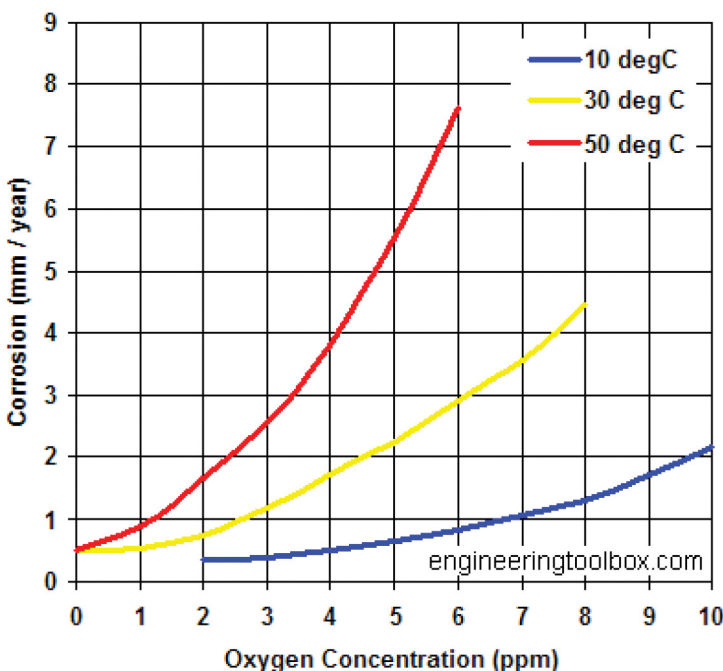


FIGURE 16: Effect of Oxygen Concentration and Temperature on the Corrosion of Low Carbon Steel in Tap Water

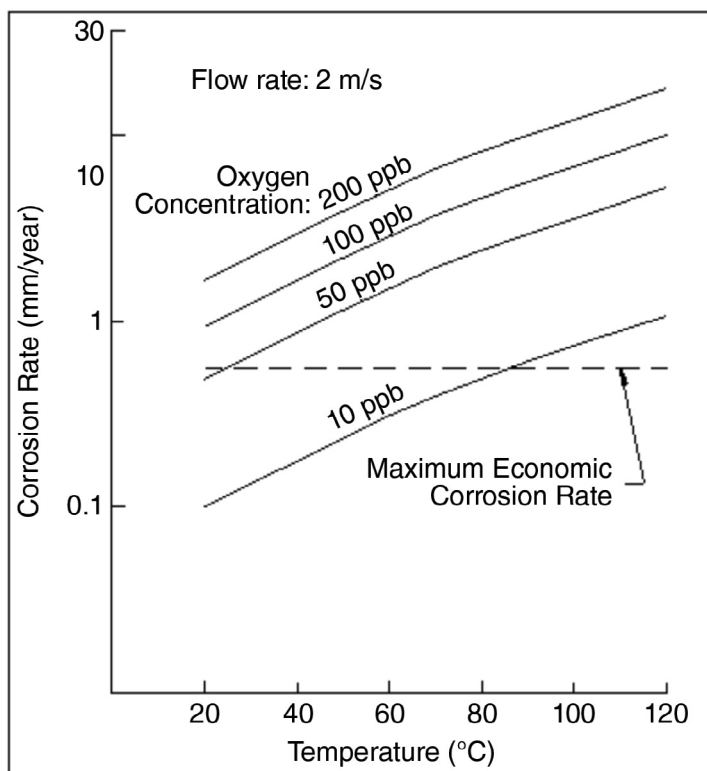


FIGURE 17: Effect of Oxygen Concentration on Corrosion of Mild Steel in Pacific Ocean Water¹⁸⁰



FIGURE 18: Oxygen Attack Occurs as a Distinctive Pit Formation

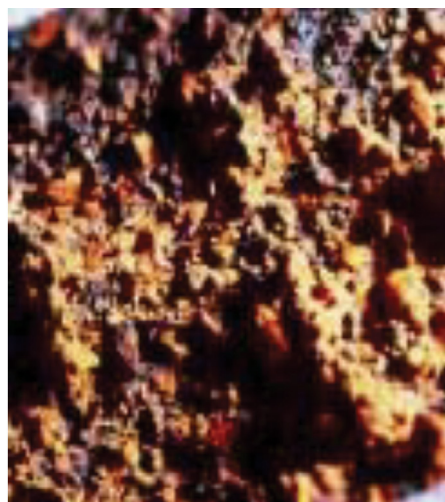


FIGURE 19: Morphology of Oxygen Corrosion

- Components such as pumps, downhole screens, chokes as well as subsurface safety valves are particularly at risk of erosion corrosion.^{189,190} Significant wear often occurs over very short time frames (days or weeks are plausible), especially if violent outbursts of episodic sand erosion occur. In gas wells, the erosion corrosion sometimes results from the impingement of mixtures of corrosive liquid droplets.¹⁹¹ Sand is increasingly produced as the reservoir pressure declines, or during water flooding of non-consolidated formations, causing water washes away of the formation with the result of an ever increasing erosion rate.
- Systems used to contain, transport and process erosive mineral slurries. This is particularly important for the oil sand industry, where handling and processing of silica-based tar sands result in severe erosion corrosion problems.^{192,193}
- CO₂ injection systems for enhanced oil recovery. Severe corrosion of carbon steel has been experienced in CO₂-saturated environments.¹⁹⁴ An iron carbonate (FeCO₃) scale, often called siderite, sometimes forms, which provides protection to some extent. However, production fluids with high velocities and in the presence of sand particles potentially damages and/or removes the protective scale, leading to a significant increase in the corrosion rate.¹⁹⁵ Partial removal of the siderite is dangerous, since the scale sometimes behaves like a cathodic surface, leading to pitting damage of the immediately adjacent bare steel, which serves as a galvanically connected anodic surface.

Understanding, predicting, and mitigating erosion corrosion is commonly handled with the cooperation of experts and engineers in related areas such as fluid dynamics, corrosion/materials engineering, chemical engineering and mechanical engineering, as indicated by review articles from different perspectives. The following sections provide a brief overview of the current understanding of erosion corrosion mechanisms and the evaluation of erosion corrosion with an emphasis on synergistic effects.

Flow Regimes

The large variety of flow regimes possible depends on a multitude of variables often best expressed using non-dimensional parameters such as the Reynolds number (Re) and the Froude number (Fr) to help characterize aggressive erosive flow patterns, and enable important comparisons between different sizes and geometries of pipeline. Other factors which are considered are average wall shear stress, maximum shear stress at the leading edge of slug and churn flows, water chemistry of the water phase, presence of organic acids, the effects of inclination, onset of water drop-out phases, gas phase products, and propensity for top of the line (TOL) corrosion. Figure 19 illustrates the complexity of flow regimes encountered in the upstream oil and gas industry.

Multiphase flow involving liquid and gas mixtures (typically oil, water, gas) is complex and still the focus of applied research. Interaction with corrosion and erosion mechanisms adds to the complexity. Liquid holdup and slippage in a system are key variables in addition to pressure drop that influence hydraulics. The amount of liquid in a multiphase system, the operating flow rate, fluid properties and the system geometry determines the flow regime of the fluid. The flow regime is a key operational factor influencing many aspects such as: pressure drop, operability, dynamic behavior, heat transfer, corrosion, chemical distribution, hydrates, wax formation, asphaltenes, scale, sand etc. Vertical pipe flow regimes such as for risers (e.g., steel catenary risers [SCRs]) are more complex, often evolving out of horizontal flow.

Multiphase Flow in Oil and Gas Pipelines

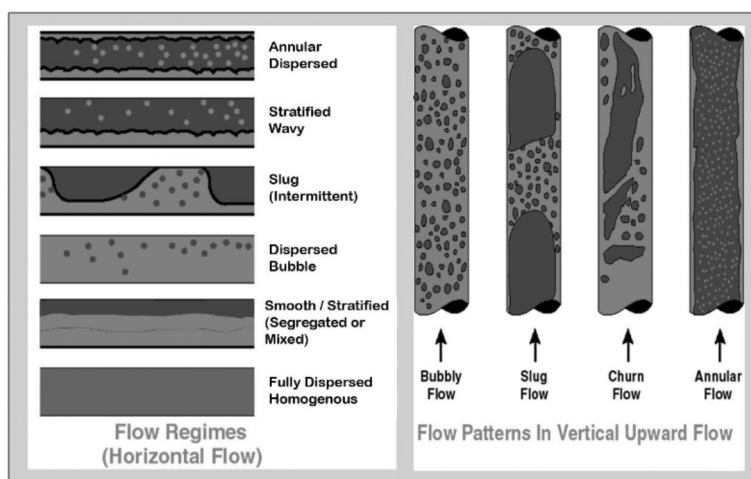


FIGURE 20: Multiphase Flow Representations for Upstream Flow Lines²⁰⁰⁻²⁰³

These flows result in various mechanical forces that potentially result in flow enhanced corrosion or erosion corrosion. Heitz²⁰⁴ summarized the sources of the various mechanical forces that cause erosion corrosion:

1. Turbulent flow, fluctuating shear stress and pressure impacts
2. Impact of suspended solid particles
3. Impact of suspended aggressive liquid droplets in high-speed gas/oil flow
4. The violent collapse of vapor bubbles in cavitation processes

The sources of the mechanical forces mentioned above are found in oil and gas production and refining systems, leading to different damage mechanisms, as indicated in Figure 20. The fluids that induce erosion corrosion are typically single phase, such as potable water, or multiphase flows, such as various combinations of gas, oil, water, and sand in the petroleum industry.²⁰⁵ It is well known that turbulent flow, fluctuating wall shear stress, and pressure impacts are sources of flow accelerated corrosion in oil and water pipelines, whereas the violent collapse of vapor bubbles in pumps and valves results in cavitation erosion corrosion.^{206,207}

The more common forms of flow enhanced corrosion and erosion include:

- Flow Enhanced Corrosion (also referred to as Flow Assisted Corrosion [FAC], or Flow Induced Localized Corrosion [FILC]): This mechanism refers to an acceleration of the corrosion process resulting from flow turbulence and disturbed flow conditions that promote the movement of corroding species, such as dissolved oxygen, to the surface and corrosion products from the surface. Flow enhanced dissolution is controlled by mass transport (see Figure 21).
- Erosion: Normally refers to the physical degradation of surfaces by the direct impaction of particulate matter such as sand, grit, corrosion products, etc. The mechanism is considered a gouging type effect without any electrochemical component.
- Impingement: Normally refers to the physical degradation of surfaces by the direct impaction of fluids alone, without the assist of any particulates, and without any electrochemical component. The results are also expressed as a liquid gouging type effect.
- Cavitation: This type of damage is the result of the implosion of gas bubbles at the metallic surface as the fluids undergo extreme changes in pressure, such as what is typically experienced at choke assemblies, impellers, etc.

These are not always clear-cut definitions since actual mechanisms are invariably mixed. Nevertheless, they are used to appropriately describe the dominant mode of degradation. Where a mix of mechanisms exists, the preferred convention is to use the dominant degradation mechanism term first. Examples are erosion-corrosion (erosion is dominant but corrosion also occurs), cavitation-erosion (cavitation is dominant but erosion also occurs), corrosion-erosion, cavitation-corrosion, impingement-corrosion, impingement-erosion etc. The term erosion corrosion has also been used in a more general connotation, encompassing a wide range of flow-induced corrosion. As such, flow enhanced corrosion, impingement and cavitation are different forms of erosion corrosion. Furthermore, it is possible, though rare, for more than two mechanisms to be occurring simultaneously. This is sometimes the case with choke sleeve damage phenomena, which occasionally reveals a dangerous combination of erosion-impingement-cavitation. Combination effects are either synergistic or antagonistic, where synergy is observed when mechanisms work in the same direction and antagonism is seen when mechanisms work in an opposing manner. This is discussed in more detail in the following section.

Erosion Corrosion and Synergies

The mechanisms of flow accelerated corrosion relate to the destruction and formation of protective films. Protective films fall into two categories: the relatively thick porous diffusion barriers formed on carbon steels (red rust) and copper alloys (cuprous oxide), and the thin invisible passive films on stainless steels, nickel alloys and other passive metals like titanium. A spectrum of erosion corrosion processes was summarized by Poulson and is presented in Table 18.

The erosion corrosion mechanisms of passive metals in flowing slurries are much more complicated than those shown in Table 18. For example, mechanical erosion usually constitutes a major part of the total material loss of stainless steels in marine pumping applications where solid erodent is present, although the protective

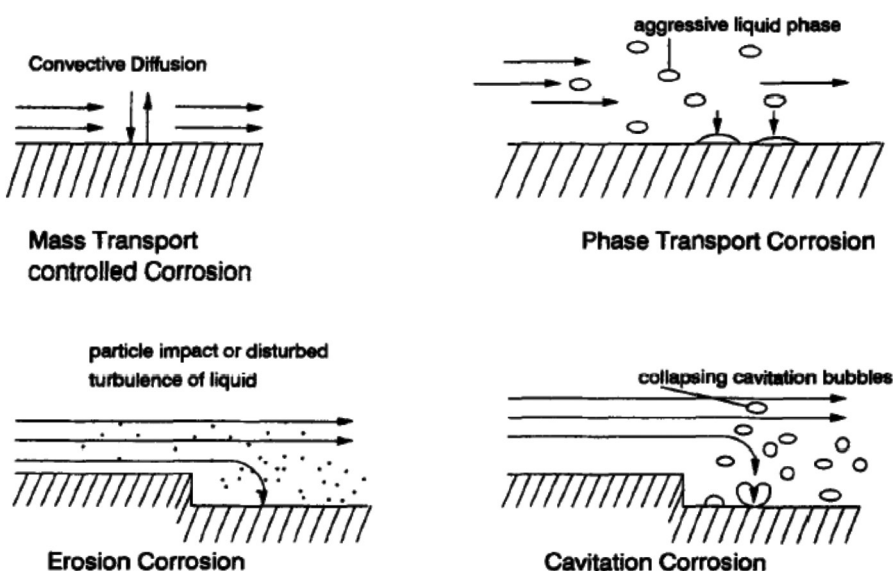


FIGURE 21: Damage Mechanisms in Corrosive Fluids²⁰⁸

Table 18
Spectrum of Erosion-Corrosion Processes

Electrochemical dissolution dominated	
Mechanism	Erosion corrosion rate
Fluid flow thins the protective film to an equilibrium thickness which is a function of both mass transfer and growth kinetics.	The metal loss rate is very low and it is controlled by the dissolution of the protective film.
Film is locally removed by dissolution, fluid induced stress, or particle/bubble impact and repassivation occurs simultaneously.	The erosion corrosion rate is a function of the rate of film removal, the bare metal dissolution rate and the subsequent repassivation rate.
Film is removed and does not reform.	It is equal to the dissolution rate of bare metal.
Film is removed and underlying metal surface is mechanically damaged, which contributes to the overall metal loss.	It is the sum of the dissolution rate of bare metal and the possible synergistic effect of mechanical damage.
Film is removed and mechanical damage to the underlying metal is dominant damage mechanism.	The direct contribution of corrosion is relatively small.
Mechanical damage dominated	

film is most times only partially removed. A large amount of experimental data has indicated that even if the corrosion component is very small (e.g., less than 5% of the pure mechanical erosion rate in the absence of corrosion), the resulting erosion corrosion rate is sometimes much greater than the metal loss rate without corrosion.²⁰⁹⁻²¹³

At reservoir sites, implementation of sand production controls, such as gravel-packing completion, has resulted in a much reduced solids loading. However, some reservoirs still produce sand up to 5 pounds per thousand barrels, which still leads to considerable material loss because of erosion. The presence of wet CO₂ corrosion sometimes increases the erosion rate of the C-Mn steel by a factor of 2-4. The corrosion rate has also been found to increase significantly, because of damage to and removal of the protective scale by the sand impingement.

Material loss can also be a function of the controlling mechanism and the exposure time. Excluding the effect of sand degradation (where smoother particles result in a reduced erosion rate with time), the erosion rate under given hydrodynamic conditions was found to be independent of time.²¹⁴ However, the erosion rate resulting from a cavitating liquid or impingement of liquid droplets has been shown to be a function of time with an initial incubation time during which the rate of material loss was negligible. Following the incubation time, the rate of material loss increased rapidly, reached a peak value and then gradually reduced to a steady value.^{215,216}

As mentioned above, two different material loss mechanisms are involved in erosion corrosion of metals: mechanical erosion and electrochemical corrosion. Mechanical erosion relates to plastic deformation and rupture of the surface layer. Small pieces of metal are removed from the surface by various mechanical forces after which the metal can dissolve into the solution. Electrochemical corrosion relates to the dissolution of metal, where the metal enters the slurry after it is ionized. The total erosion corrosion rate ECR is the sum of the material loss rates caused by erosion and corrosion $\dot{c}$, as shown in Equation (62):

$$ECR = \dot{e} + \dot{c} \quad (62)$$

The total material loss in corrosive fluids is normally larger than the sum of pure mechanical erosion $\dot{e}_0$ and pure electrochemical corrosion $\dot{c}_0$. According to ASTM G119, the pure mechanical erosion is defined as the erosion in an inert environment and the pure electrochemical corrosion is the corrosion under erosion-free conditions. The additional wastages of erosion and corrosion components caused by synergistic effects are regarded as the corrosion-enhanced erosion $\dot{e}_c$ and the erosion-enhanced corrosion $\dot{c}_e$.²¹⁷ This is shown in Equations (63) and (64):

$$\dot{e} = \dot{e}_0 + \dot{e}_c \quad (63)$$

$$\dot{c} = \dot{c}_0 + \dot{c}_e \quad (64)$$

The erosion-corrosion mechanism is affected by all factors that control corrosion and all factors that affect erosion. In combination, the damage is synergistic and can be extremely aggressive. In Equation (65) the synergism of erosion and corrosion, $\dot{s}$, is expressed as the sum of $\dot{e}_c$ and $\dot{c}_e$.²¹⁸

$$\dot{s} = \dot{e}_c + \dot{c}_e \quad (65)$$

According to experimental data summarized by Watson et al,²¹³ the synergistic contribution to the total material loss is sometimes up to 92%. Therefore, the synergistic effect is usually not ignored in the engineering assessment of equipment service lifetimes.²¹⁹⁻²²¹

The corrosion rate of erosion corrosion processes can be determined using standard electrochemical measurement procedures, such as LPR (ASTM G59) or potentiodynamic polarization (ASTM G5).²²² The pure mechanical erosion rate in corrosive slurries can be found by suppressing corrosion through the application of cathodic protection under the same hydrodynamic conditions. ASTM G119 polarizes the specimen to a cathodic potential of one volt with respect to the open circuit potential to guarantee a corrosion-free condition. However, caution is taken to avoid hydrogen embrittlement in some materials. Also, gas bubbles produced by the evolution of hydrogen occasionally affect the hydrodynamic conditions. A recent study indicated that erosion rates under cathodic protection in slurries prepared with dilute acidic solutions were much higher than those in neutral and alkaline slurries.²²³

From ASTM G119, the following dimensionless factors are defined to describe the degree of synergism:

Total synergism factor is shown in Equation (66):

$$\frac{ECR}{ECR - \dot{s}} = 1 + \frac{\dot{s}}{\dot{e}_0 + \dot{c}_0} \quad (66)$$

Corrosion augmentation is shown in Equation (67):

$$\frac{\dot{c}}{\dot{c}_0} = 1 + \frac{\dot{c}_e}{\dot{c}_0} \quad (67)$$

Erosion augmentation is shown in Equation (68):

$$\frac{\dot{e}}{\dot{e}_0} = 1 + \frac{\dot{e}_c}{\dot{e}_0} \quad (68)$$

Despite numerous efforts, it is still difficult to predict the synergism quantitatively, because many factors are involved in the erosion corrosion processes including the metallurgical features of the material, the hydrodynamics of the fluid and flow field, the characteristics of erodent, temperature, and corrosiveness of the media.²²⁴⁻²⁴⁰

Flow Enhanced Corrosion: Mass Transfer Controlled Corrosion

Mass transfer controlled corrosion is related to the transport of reactants (often dissolved oxygen) through the diffusion boundary layer to the metal surface or diffusion of a soluble corrosion product away from the surface. The mass transport kinetics in the liquid boundary layer is formulated in Equation (69):²⁴¹⁻²⁴⁴

$$Sh = \alpha Re^\beta Sc^\gamma \quad (69)$$

The non-dimensional parameters in Equation (69) are Sherwood number $Sh = K_{\text{mass}}d/D$, Reynolds number $Re = Ud/\nu$ and Schmidt number $Sc = \nu/D$; where α , β and γ are constants depending upon the flow conditions and the geometry of the test devices; K_{mass} is the specific mass transfer coefficient, d is a specific size depending on the geometry of test device; D is the diffusion coefficient of the controlling species; U is the flow velocity; and ν is the kinematic viscosity of the fluid.

Equation (77) was originally established for the rotating disk electrode (RDE) system, but was later extended to various systems, including pipelines, by equating hydrodynamic parameters and developing relationships between flow in laboratory apparatus and in pipelines.²⁴⁵ Similar corrosion rates and mechanisms are expected when the hydrodynamic parameters are the same.

In a straight pipe, d in Equation (70) represents the pipe diameter:

$$K_{\text{mass}} = \alpha D^{1-\gamma} d^{\beta-1} \nu^{\beta-\gamma} U^\beta \quad (70)$$

Under mass transfer control within the liquid boundary layer, the corrosion rate $\dot{C}$ is given by Equation (71):

$$\dot{C} = K_{mass} C_B \quad (71)$$

Where:

C_B is the concentration of controlling species in the bulk solution/slurry.

Determination of the appropriate values of the parameters in Equation 71 is difficult and approximate values are often used, especially when multiphase flow is present. Variations of hydrodynamic parameters along the pipeline in addition to surface roughening because of corrosion, or the occurrence of film formation further complicate the use of Equation (71) for the prediction of corrosion rates. For example, the pipe surface roughness can affect the β value, which usually ranges from 0.5 to 1 for mass transfer controlled corrosion.²⁴⁶

In the presence of a protective corrosion product layer, the apparent mass transport coefficient is formulated in Equation (72):²⁴⁷

$$\frac{1}{K_{mass}} = \frac{1}{K_B} + \frac{1}{K_F} \quad (72)$$

Where:

K_B and K_F are the mass transport coefficients in the solution boundary layer and the corrosion product film, respectively.

For a passive metal, mass transfer through the passive film is much slower than in the liquid phase, $K_B \gg K_F$, and $K_{mass} \approx K_F$. With the passive film intact, the corrosion of iron-based alloys is controlled by the diffusion of oxygen vacancies within the passive film and, therefore, by the oxygen vacancy density within the passive film.²⁴⁸ Fluid flow and turbulence sometimes increases the dissolved oxygen supply to the metal surface, leading to a reduced oxygen vacancy density in the passive film and, subsequently, a reduced corrosion rate. If the fluid damages and/or destroys the passive film, the corrosion rate increases dramatically.²⁴⁹

Corrosion under Mixed Mass Transport and Kinetic Control

It has been found that the linear relationship of Equation (79) is not always valid. Generally, $\dot{C} \propto K^m$. The deviation of m from 1 suggests that the corrosion reaction is not fully under mass transfer control, as illustrated in Figure 21.

Many experimental investigations have indicated that the mechanical forces of fluid flow play an important role in CO_2 and/or H_2S corrosion in oil and gas production.²⁵⁰⁻²⁵³ According to De Waard et al, CO_2 corrosion is under mixed mass transport and kinetic control, so that the apparent corrosion rate coefficient K is given by Equation (73):

$$\frac{1}{K} = \frac{1}{K_r} + \frac{1}{K_{mass}} \quad (73)$$

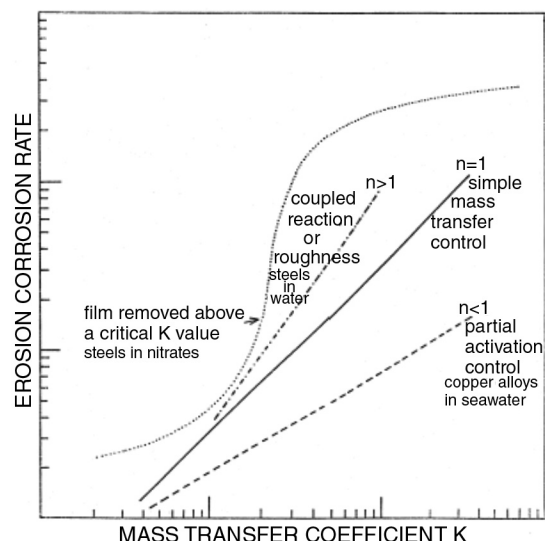


FIGURE 22: Possible Relationships Between the Erosion Corrosion Rate and The Mass Transfer Coefficient

Where:

K_r and K_{mass} are associated with interface corrosion reaction kinetics and mass transfer of dissolved CO_2 from the bulk solution to the pipe wall

The value of K_{mass} can be estimated using Equation (81). When $K_r \gg K_{mass}$, the corrosion reactions are solely controlled by mass transport, $K = K_{mass}$. Under kinetic control with very fast mass transport, $K_{mass} \gg K_r$ and $K = K_r$. The corrosion rate is equal to $\dot{C} = K [\text{CO}_2]$, where $[\text{CO}_2]$ is the CO_2 concentration in the bulk solution and is proportional to the partial pressure of CO_2 .

K_r is a function of steel composition and microstructure, temperature, and solution chemistry including CO_2 concentration, water cut, pH etc. Because it is relatively simple, the De Waard model has been widely used in CO_2 corrosion rate prediction.²⁵⁴ CO_2 corrosion often results in the formation of a corrosion product scale that has a protective function to some extent. In the De Waard model, the mass transfer in the corrosion product scale is not taken into account, although many enhancements and refinements continue to be made to such models. Re-

cently, the research group led by Nesic developed an integrated model to predict the CO₂ corrosion rate.²⁵⁵ In Nesic's model, the dependence of corrosion reactions on the over potential were assumed to obey Butler-Volmer-type equations that are dependent on the composition and microstructure of steels, as well as on solution chemistry. They used the generalized Fick's Law to describe the mass transport kinetics. To take the effect of diffusion in the surface scale into account, Nesic et al introduced the concept of turbulent diffusion. It is assumed that mass transport in the liquid boundary layer is affected by both conventional diffusion and turbulent diffusion, while mass transport within the corrosion product scale is only affected by conventional diffusion caused by a concentration gradient. The turbulent diffusion coefficient D_t is a function of the distance from the metal surface x , the thickness of the corrosion product scale δ_p , and the thickness of the liquid boundary layer δ . δ can be calculated directly if the Reynolds number and pipe diameter are known. In Nesic's model, the surface film formation kinetics is related to precipitation resulting from chemical reactions in the solution. The concept of surface coverage was used to formulate the effects of H₂S traces and inhibitors. When mild steel is exposed to a corrosive fluid containing CO₂, the thickness of corrosion product scale sometimes increases slightly for flow velocities in the range of 0.1 m/s to 20 m/s, but the thicker scale is less protective because of a higher porosity.²⁵⁶ When Nesic's models are used, computer simulation is used to incorporate the fluid dynamics of multiphase flow together with corrosion kinetics.²⁵⁷

The basic concepts used to build predictive models for H₂S corrosion are similar to those used to predict CO₂ corrosion. In both cases, corrosion product scales form via certain precipitation mechanisms. Because the affinity of H₂S to iron is very high, the formation of mackinawite scale is much faster than the formation of ferrous carbonate (siderite) film.²⁵⁸ When a small amount of H₂S is present in an environment (typically < 10 to 20 ppm) with CO₂ corrosion, protection by the corrosion product scale is improved. If the H₂S concentration exceeds a certain critical value (possibly between 20 and 50 ppm), a further increase in H₂S enhances pitting corrosion.²⁵⁹

Other allotropes of iron sulfide and iron carbonate are thought to also exist, however the predominant forms, certainly in upstream applications, are mackinawite and siderite, and both tend to exhibit corrosion accelerating galvanic tendencies with respect to bare steel. The challenge for the engineer is to identify the exact nature of the scales, if possible, to help with the corrosion prediction analyses. That is usually done by an X-ray compound analysis of the suitably scraped off scales from the surfaces in question. If removable coupons have been used, an SEM analysis of the surface morphology also helps verify the role of erosion type phenomena. X-ray and SEM analyses are established techniques commonly available at local commercial laboratories or regional universities for fairly modest fees. The data usually prove to be invaluable in helping to identify the problem and formulate the solutions.

Critical Impingement Velocity

The exact mechanism of protective film damage during erosion corrosion in single-phased turbulent flow is still unclear. In corrosive fluids, the removal of a protective film is generally related to the mechanical forces of fluid flow, chemical dissolution, and their synergism.²⁶⁰⁻²⁶² There is uncertainty regarding the individual roles of mechanical forces and mass transfer in film disruption since both of them are directly related to turbulence intensity.^{263,264} Generally, high turbulence resulting from high flow velocities leads to a breakdown of protective films.

Based on experience in the electric power industry with erosion corrosion of carbon steel by steam condensate, API RP 14E265 lists an empirical formula, shown below in Equation (74), to estimate the critical velocity (ft/s) beyond which the corrosion rate becomes unacceptably high as a result of the onset of erosion corrosion:

$$U_e = \frac{C_{API}}{\sqrt{\rho_m}} \quad (74)$$

Where:

ρ_m is the density of the gas/liquid mixture in lb/ft³.

C_{API} is a constant.

The C-Factor as it is more commonly known is an important first pass parameter used to define the allowable flow rates for a particular system. A C factor value of 450 is typically used for seawater injection systems constructed from corrosion-resistant alloys. Oil and gas multiphase flows tend to invoke a C-factor of 120 -150 if there are minimal sand or particulates in the pipe inventory. If the risks of corrosion and/or erosion are more tangible, then a C-factor of 100 is typically more appropriate, and this is potentially the case for other materials, such as the CRAs. If inert or inhibited systems are deployed then C-factors of 150-200, and beyond are sometimes deployed.

Liquid jet impingement tests on carbon steels and 12Cr steels indicate a considerably higher erosion corrosion resistance in the absence of solid particles than that predicted by API RP 14E. This is potentially partly attributed to an effect of environment and system geometry, which also have an impact on the critical velocity. Efforts have been made to modify Equation (13) to provide a more universal C_{API} factor, by taking the hardness of surface films into account.²⁶⁶ Because the protective film (passive film or corrosion product

Table 19
Wall Shear Stress and Adherence of Corrosion Product Scales to Steel Substrate

Service condition	Wall shear stress (Pa)	Type of scale	Adherence of scale (Pa)
Typical systems	10 ⁰ to 10 ²	High porosity scale	10 ⁷ to 10 ⁸
Region with high turbulence	10 ⁴ to 10 ⁵	Low porosity scale	10 ⁸ to 10 ⁹

scale) is very thin (~10 nm or less), both theory and experimental techniques for evaluating the mechanical properties of the protective film are not well established.²⁶⁷

The critical velocity can be regarded as the critical condition leading to passive film breakdown and, therefore, it is a useful tool

to evaluate the erosion corrosion susceptibility of materials under impinging liquid droplets in high velocity gas flow. However, it does not relate to the corrosion rate after passive film breakdown.

Wall Shear Stress and Turbulence Intensity

Efird proposed the concept of 'critical wall shear stress' for the disruption of corrosion product scale. The wall shear stress τ_w produced by fully developed pipe flow in a straight pipe is formulated in Equation (75):²⁶⁷

$$\tau_w = \frac{\Delta P}{4x/d} = f \frac{\rho_m U^2}{2} \quad (75)$$

Where:

f is the Fanning friction factor²⁶⁹

The Moody chart provides friction factors as a function of the Reynolds number and surface roughness. A wall shear stress exceeding a critical value $\tau_{w,crit}$ causes disruption of the corrosion product scale. Efird et al used the wall shear stress as a hydrodynamic parameter to predict flow-induced corrosion in Equation (76):

$$\dot{c} = a \tau_w^b \quad (76)$$

Where:

a and b are experimental constants.

Equations have been developed that use the wall shear stress to correlate the corrosion rates measured with the rotating cylinder electrode (RCE) system and pipe flow, and those measured with the RCE and jet impingement systems.^{270,271} The applicability of this concept downstream of sudden geometric changes, where detached flow is present, is still being tested.^{272,273} Field experience has indicated that the most severe erosion corrosion problems occur under conditions of detached turbulent flow at sudden changes on the flowing system, such as bends, heat-exchanger-tube inlets, orifice plates, valves, fittings and in turbo-machinery including pumps, compressors, turbines and propellers.

An effort has been made to correlate wall shear stresses directly to the disruption of corrosion product scale and protective inhibitor films in CO₂ and H₂S corrosion of carbon steel.²⁷⁴⁻²⁷⁶ The existence of a critical wall shear stress for disruption of corrosion product scale and initiation of flow-induced localized corrosion has been demonstrated experimentally.^{277,278} However, as indicated by the data in Table 17, the calculated hydrodynamic forces applied by wall shear stresses are orders of magnitude lower than those for the destruction and spalling of scales on a pipe wall.²⁷⁹ This would imply the presence of certain hydrodynamic forces that correlate to the wall shear stress and that are capable of physically removing corrosion product scale.

In parallel, various modeling studies have tried to correlate actual wall shear stresses to film removal and implicit corrosion rates at the wall, but success has been limited. As a rule of thumb, the following risk based guidelines are used:

- Fluid Shear Stress < 50 Pa Minor effect on scale removal Low Risk Erosion
- Fluid Shear Stress 50-100 Pa Small effect on scale removal Low/Medium Risk
- Fluid Shear Stress 100-500 Pa Significant effect Medium/High Risk
- Fluid Shear Stress > 1000 Pa Major effects on scale removal High Risk

While investigating the forces used to remove corrosion product scale, Schmitt et al. observed fluctuating shear stresses and pressures at the surface with high forces obtained during quasi-cyclic bursting events. It was proposed that the turbulence intensity I_{turb} (Pa)

could serve as a hydrodynamic force in the disruption of the corrosion product scale. The turbulence intensity was defined as the intensity of momentum transfer by near-wall turbulence elements (vortices) to the wall in Equation (77):

$$I_{turb} = \frac{P_V}{T_C A_V} \quad (77)$$

Where:

P_V (Nm) is the momentum transferred by a single burst of turbulence elements to the wall (single burst)

T_C (s) is the time interval between the burst events that is inversely proportional to wall shear stress

A_V (m²) is the surface area impacted by a single burst.

According to Schmitt et al., the critical condition for disruption of corrosion product scale is shown in Equation (78):²⁷³

$$I_{turb} \geq \sigma_{ff} = E_f \epsilon_{ff} \quad (78)$$

Where:

σ_{ff} is fracture stress

E_f Young's modulus.

ϵ_{ff} is the critical fracture strain of scale.²⁸⁰

Hence, the critical wall shear stress leading to localized disruption of corrosion product scale is correlated to the fracture stress of scale as follows in Equation (79):²⁸¹

$$\tau_{w,crit} = K_V \sigma_{ff} \quad (79)$$

K_V is a function of hydrodynamic parameters including the mass of the near wall turbulence element, the streamwise vortex velocity, the density and viscosity of vortex etc. The concept of turbulence intensity has been used by Schmitt et al. in modeling the probability of flow induced localized corrosion of carbon steels in sweet and sour environments. The ex situ mechanical properties of corrosion product scale are measured with fracture mechanics experiments. It is worthwhile to point out that dehydration of the corrosion product scale likely occurs when the mechanical properties are measured ex situ and this dehydration has the potential to alter the mechanical properties. Unfortunately, little data has been reported on the mechanical properties of scales when measured using in situ techniques.

Corrosion of Passive Metals in Flowing Slurries

When the kinetic energy of solid particles in flowing slurries exceeds a threshold value, particle impingement produces a small crater in the passive film. This leads to a sharp rise of the local corrosion current over the crater surface followed by current decay with time as a result of repassivation. Consequently, the corrosion current density is no longer uniform over the impacted surface. The average corrosion current density depends on the rate of passive film removal and repassivation kinetics.²⁸² The latter is determined using a single particle impingement or a scratch test.^{283,284} Equations have been established that allow, subsequently, for the determination of the corrosion augmentation as defined by ASTM G119. It has been demonstrated that this approach provides a good prediction of pipeline steel corrosion current densities. Figure 22 illustrates the same good prediction for UNS S30400 (Type 304 stainless steel) in flowing slurries.

Erosion and Corrosion-Enhanced Erosion

Many mechanistic models have been developed for mechanical erosion.²⁸⁵⁻²⁸⁸ In flowing slurries, the overall dependence of the erosion

rate on the particle and target hardness (H_p and H respectively) is approximately given by $\dot{e}_0 \propto H_p^{1/2} / H$ over a fairly wide range of variables.²⁸⁹ Generally, the erosion resistance of target materials increases with their hardness if no substantial change takes place in the erosion mechanisms. As illustrated in Figure 23 and Equation (80), a power law erosion rate of materials gives a fairly good prediction of the erosion rate based on the substrate hardness.²⁹⁰

$$\dot{e}_0 = \kappa_H H^{-n_H} \quad (80)$$

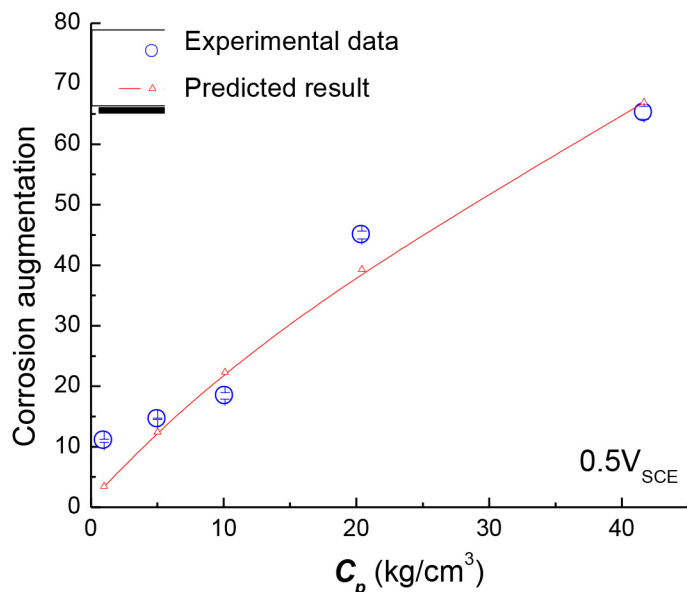


FIGURE 23: Comparison of Predicted and Experimental Corrosion Current Densities of UNS S30400 (Type 304 Stainless Steel) under Slurry Impingement (Slurry: Tap Water + Sand, Impingement Velocity: 5 m/s, Impingement Angle: 90°)

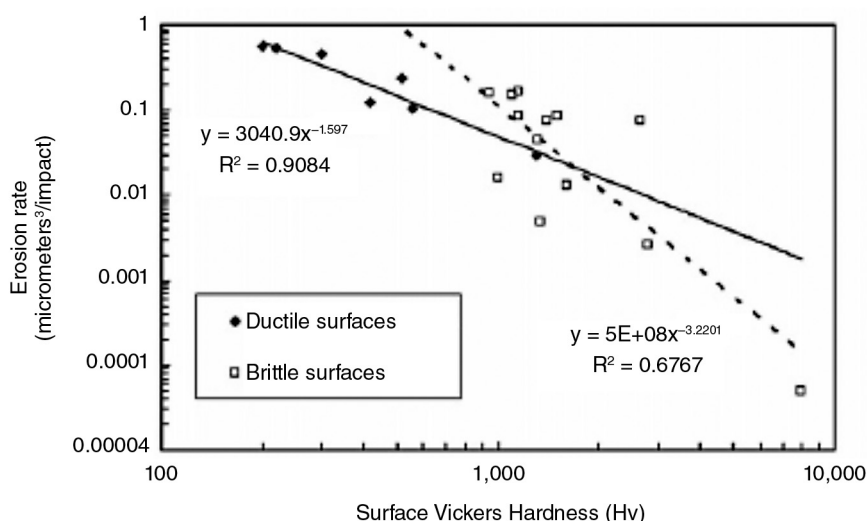


FIGURE 24: Dependence of Erosion Rate on the Surface Hardness

wall thickness using commercially available computer controlled techniques. The topographical map obtained presents a real time pattern of the wall thinning distribution. Repeat mapping scans, e.g., every three, six, or 12 months, provides a very useful picture of the way erosion mechanisms are behaving, and thus facilitate responsive actions that are sometimes done.

Prediction of Erosion Corrosion: Dependence on Flow Velocity

Although many efforts have been made to establish a theoretical model to predict the performance of engineering components based on erosion corrosion experimental data obtained in the laboratory, limited progress has been made, mainly because the prediction, particularly in multiphase flow, is highly complicated. Different flow patterns are encountered in multiphase flow depending on the gas, liquid and solid flow rates, pipe size, inclination angles and fluid properties. Additional parameters that affect the erosion severity are solids loading, solid particle properties, pipe wall material, and pipe geometry or fitting.²⁹³⁻²⁹⁵ Erosion corrosion prediction models are largely based on empirical equations determined from experimental data, so that they only apply to operating conditions that are similar to the experimental conditions. The following example (Equation [81]) is an equation that correlates the erosion corrosion rate (ECR) to flow velocity, U , (see also Equation [70] and Equation [71]).²⁹⁶

$$ECR = \text{const.} \cdot U^{\beta} \quad (81)$$

Where:

κ_H and n_H (> 0) are experimental constants that depend heavily on the erosion mechanisms.

Electrochemical corrosion has been observed to result in the degradation of surface hardness. Microhardness and nanoindentation techniques have been used as in situ techniques to demonstrate the effect of corrosion on carbon steels and commercially pure iron.^{291,292} Figure 24 illustrates that the decrease in the normalized hardness becomes more substantial at the higher anodic current densities. The subsequent increase in the erosion rate is defined as corrosion-enhanced erosion and the erosion augmentation is determined from experimental data.

Erosion Corrosion Maps

Stark produced erosion-corrosion maps to demonstrate correlations between erosion corrosion mechanisms, the performance of materials, and process parameters such as temperature, potential, flow velocity, particle concentration, impact angle etc.²⁸⁵ Figure 25 provides examples of erosion corrosion maps that illustrate the dependence of erosion corrosion mechanisms and wastage of carbon steel in aqueous slurries on the applied potential and flow velocity. Although convenient, these maps do not capture the many factors related to mechanical, chemical, and material aspects that affect the erosion corrosion behavior of material. Furthermore, the interactions of these factors are very complicated, which are difficult to demonstrate in a few maps. Stark et al²⁸⁶ made efforts to group various parameters into dimensionless ones and to build the erosion corrosion maps using these dimensionless parameters. However, more work is being done to understand the physical meanings and the universal applicability of these non-dimensional parameters. In practice, erosion or corrosion maps are created by the use of on-line ultrasonic mapping, whereupon the surface of interest (pipe, riser, vessel, etc.) is 'gridded' out and mapped for

The β value on the relative contributions of corrosion and erosion to the total material loss and is often used as a diagnostic tool for the erosion corrosion mechanism, as summarized in Table 20.

In flowing slurries, it is generally believed that corrosion dominates the material loss if β is close to 1 and that erosion dominates the material loss when β is close to 3.²⁹⁷ However, for charge transfer controlled corrosion, both theoretical analyses and experimental results have indicated that the anodic dissolution current density increases linearly with the extent of plastic deformation induced by the impingement of solid particles.^{298,299} Further promoted by increasing impingement velocity and sand concentration, the β -value is likely to be larger than zero. When corrosion is controlled by the repeated breakdown of passive films because of particle impingement and repassivation, the β value is close to 3, as shown in Figure 26.

Erosion Models

Concerns regarding the predicted values obtained from API 14E have resulted in the development of a number of other “erosion” models. API 14E often results in overly conservative predictions and these other models are attempts to obtain a more soundly based and justifiable erosion rate prediction. Some of the best-known models that have been developed are those of Salama,²⁹² Kvernfold,²⁹³ and Shirazi et al (Tulsa University),²⁹⁴ Other models have been previously produced but are no longer actively developed.

The AEA model has been developed from an empirical approach in churn and bubbly flow regimes. The other models were derived via a theoretical route, but have experimental verification. Two models account for particle trajectories, based on either empirical formulas or actual calculations. All three models incorporate a general erosion equation, shown below as Equation (82), which is a function of particle impact velocity:

$$\dot{e} = AV_p^n F(\alpha) \quad (82)$$

Where:

A and n are experimentally determined constants that depend on material properties

V_p is the particle impact velocity

$F(\alpha)$ is a function that depends on the impact angle.

The value of n lies between 1 and 3 for ductile materials but varies between the models. The differences between the models lead to significant differences between predicted erosion rates (up to two orders of magnitude), which sometimes show certain operating conditions acceptable by one model, but unacceptable by another. There are limitations of such models and typically, the two models are used to select the highest predicted erosion rate.

A more comprehensive approach to erosion modeling includes modeling of the fluid flow as well as particle trajectories, which uses computational fluid dynamics (CFD).^{301,302} This is not a simple task and time consuming, especially in the presence of multiphase flows. A CFD-based model has been used to predict the effects of flow patterns on the material loss rate in geometries such as elbows and tees.

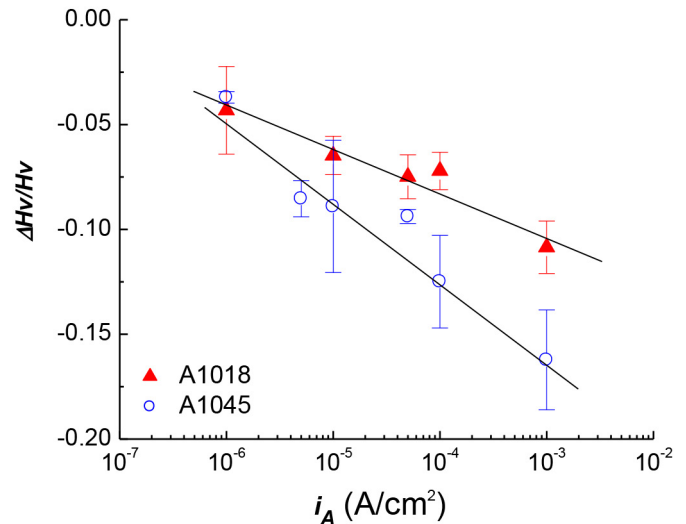


FIGURE 25: The Normalized In-Situ Hardness Drops with an Increase in The Anodic Current Density

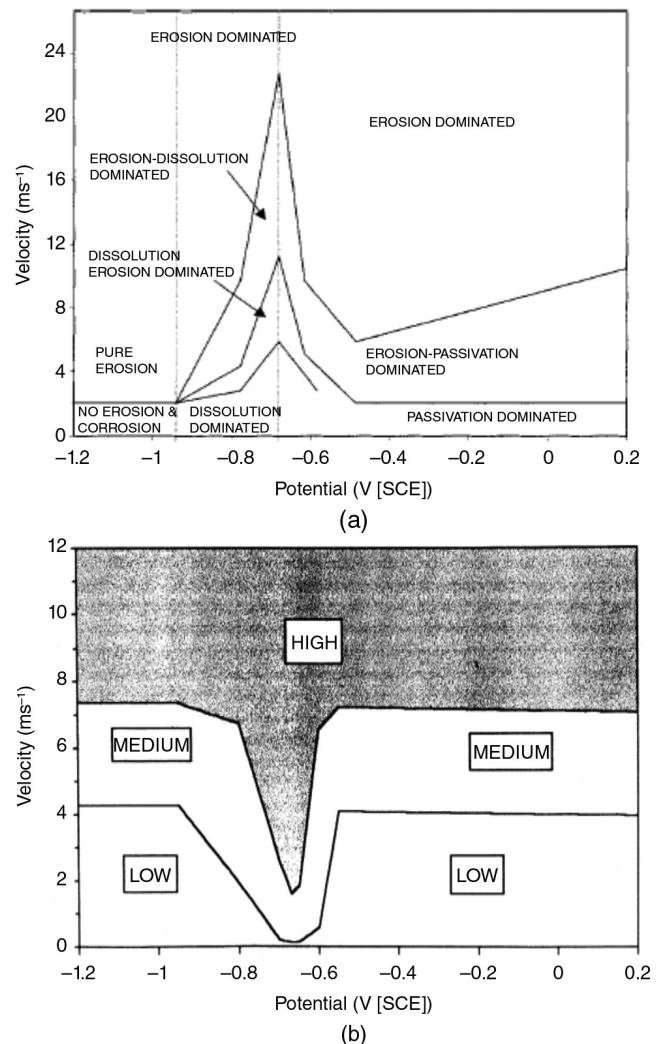


FIGURE 26: Erosion Corrosion Maps for Mild Steel in Carbonate/Bicarbonate Slurries Displaying (a) Mechanisms and (b) Wastages where High: $\dot{e}\dot{c} > 10$; Medium: $1 < \dot{e}\dot{c} \leq 10$; Low: $\dot{e}\dot{c} \leq 1$

Table 20
 β Value and Erosion Corrosion Mechanism Summarized
by Heitz and Postlethwaite et al^{204, 300}

Mechanisms of material loss	Postlethwaite et al	Heitz
Corrosion		
Liquid-phase mass transfer control	0.8 to 1	0.33 to 1
Charge transfer control	0	-
Mixed charge/mass transfer	0 to 1	0 to 1
Activation/repassivation	1	-
Erosion		
Solid-particle impingement	2 to 3	0.5 to 3
Liquid droplet impingement in high speed gas flow	5 to 8	5 to 6
Cavitation attack	5 to 8	2 to 12

None of the discussed erosion models include the effects of corrosion. In addition to specific erosion models, corrosion models are used to give corrosion rate predictions in flowing conditions but also have limitations in predicting losses when flow rates and sand loadings are high.

Mitigation Strategies of Erosion **Corrosion: Engineering Design**

Careful design of flow geometry usually effectively minimizes turbulence intensity, especially that caused by disturbed flow at weld root protrusions and flange steps. Design measures often include: running piping as directly as possible with the number of bends kept to a minimum, optimization

of elbow bend radii, gradual changes in flow cross-sections, and replacement of an elbow with a plugged tee.³⁰³

It has been suggested that optimal bend ratios (bend radius/tube diameter) is generally in the range of 2 to 4. For susceptible materials, higher bend ratios are typical. Lower bend ratios are used with resistant materials, particularly in large diameter lines.

The number of branch connections is generally kept to a minimum. As with bends, the greatest root radius possible is used. The use of swept branches is common and in fabricated pipe branches particular care is taken to maintain a smooth transition into the branch.

Particular care is taken at pipe connections to avoid misalignment between the components.

Valves are potential turbulence raisers. Where possible, flow paths through the valves are kept as straight as possible. It is also typical to install straight lengths of pipe downstream of valves to allow stable flow to be re-established quickly.

The collection of entrained air within a system usually influences the severity of impingement attack. Fittings to release air from high points in the system are generally provided where feasible.

Utilization of helically-formed pipes to enhance the swirl flow in a pipe reduces the critical flow velocity of suspending solid particles and the erosion rate significantly. It leads to uniform erosion over the entire inner pipe surface and hence reduces localized wall penetration. Helically-formed pipes also reduce the pressure drop and improve the particle distribution across the elbow. If, at the risk of flow-induced corrosion, diffusers and collectors are used, the angle between the wall of the apparatus and the main flow direction is often less than 10°.

Increasing the thickness of materials in critical areas, the use of impingement plates to shield critical areas, or the rotation of slurry pipes extends the component's life. Sometimes, acceptance of a high erosion rate with regular inspection and replacement is less costly than the use of more expensive materials. This practice is used extensively in minerals processing and oil/gas industries. Erosion resistant coatings or deposits are also effective, particularly in pumps and valves. Cavitation corrosion is avoided by increasing the static pressure in the flow systems. An increase by a factor of 2 or 3 generally suffices.

Process design improvements sometimes include decreased particle size, lower flow velocities or slurry pH, and sand concentration control. The erosion rate is reduced significantly when the particle size is less than 100 μm .³⁰⁴ A larger β -value in Table 15 indicates a greater sensitivity of the system to flow velocity and in such a system, a reduced flow velocity is usually effective. For mass transfer controlled corrosion following the removal of a protective film, the corrosion rate is decreased by lowering the flow velocity. Cathodic protection is considered when there is sufficient throwing power.

Pitting corrosion in flowing slurries has been observed in both the field and in laboratory tests. Pitting is promoted by local defects in the corrosion product layer as a result of either non-uniform oxide growth or mechanical destruction by fluid-induced forces.³⁰⁵ An increase in the surface roughness caused by erosion sometimes promotes pitting corrosion, since a rough surface occasionally enhance localized turbulence.³⁰⁶ A low flow velocity reduces the erosion corrosion damage, but it reduces the economic output as well. Also, the flow velocity has to exceed a minimum value to keep the particle in suspension.³⁰⁷ Velocities that are too low result in sliding abrasion along the horizontal pipe bottom.

Material Selection: General Considerations

The degree of erosion corrosion depends on both the mechanical and electrochemical properties of a material. An increase in the Cr-content of steels sometimes improves the corrosion resistance and therefore the erosion corrosion resistance. It has been widely recognized that the erosion resistance of metallic materials increases with increasing relative hardness, which is the difference between the hardness of target material and particles.³⁰⁸⁻³¹⁰ This is valid as long as there is no substantial change in the erosion mechanism.^{311,312} In corrosive slurries, the total weight loss caused by slurry erosion does not decrease with an increase in hardness when the mechanism is dominated by corrosion. When removing the corrosion contribution from the total weight loss, Wang and Stack found that only the erosion resistance of mild and stainless steels increased with increasing hardness. Erosion by solid/gas mixtures also did not correlate well to material mechanical properties under quasi-static loading conditions.³¹³ It is still hard to generalize the effects of hardness, since erosion also depends on ductility and surface roughness.³¹⁴ Furthermore, chemical changes within the surface layer sometimes results in the onset of erosion-corrosion and, therefore, its stability in the process environment is just as important.

Practically minded standards and codes of practice such as those issued by the API, UK HSE⁽⁸⁾, and DNV are very useful to help understand, and predict the onset, growth of erosion related damage and provide guidelines for its mitigation.

Steels and Corrosion Resistant Alloys

Experimental data has indicated that the erosion resistance of carbon steels increases with an increase in carbon content.³¹⁵ Stainless steels are more resistant to erosion-corrosion than carbon and low alloy steels because of the high chromium content.³¹⁶ The addition of other alloy elements such as Mo, Mn, and N also improved the erosion-corrosion resistance of stainless steels.³¹⁷⁻³¹⁹ Steels with low bainitic structures are generally more resistant to erosion-corrosion than those with ferrite-pearlite structures. Duplex stainless steels and high nickel alloys have been found to be particularly resistant to wear in corrosive service.

Chrome White Irons

Chrome white irons (CWIs) have excellent abrasion resistance and moderate ability against impact, which is helpful for crushing, grinding, and slurry erosion applications.³²⁰⁻³²² It is often applied as weld hardfacing on the surface of low carbon steel pipelines to improve the erosion-corrosion resistance.³²³ Generally, a high carbon content is common for the formation of carbides to provide erosion resistance, but a minimum Cr-content of 12% in the metal matrix is typical for the corrosion resistance of the material.³²⁴⁻³²⁷ A wear and corrosion performance map is shown in Figure 27.

Metal Matrix Composites

Metal matrix composites (MMCs) are normally used as a hard coating and are comprised of a metallic binder and hard particles phases. Binder materials include Ni, Co, Al and their alloys, and sometimes austenitic stainless steel.³²⁸⁻³³¹ The hard particle phases commonly used include WC, B₄C, and SiC. Wear of the composite is mainly governed by the synergistic effect of two simultaneous processes: corrosion, erosion and abrasion of the matrix by the slurry, and fracture and removal of the hard particles because of erodent impingement at a high speed.^{332,333} The erosion-corrosion resistance of MMC depends heavily on the corrosion resistance of the binder, since the binder material tends to dissolve preferably. The hard particles are readily removed by erosion if they lose support of the binder. Nickel-chromium-cobalt grades and the nickel-chromium grades were found to improve the erosion-corrosion behavior compared to the pure cobalt grade³³⁴. Further improvements are usually obtained by optimizing the binder composition.

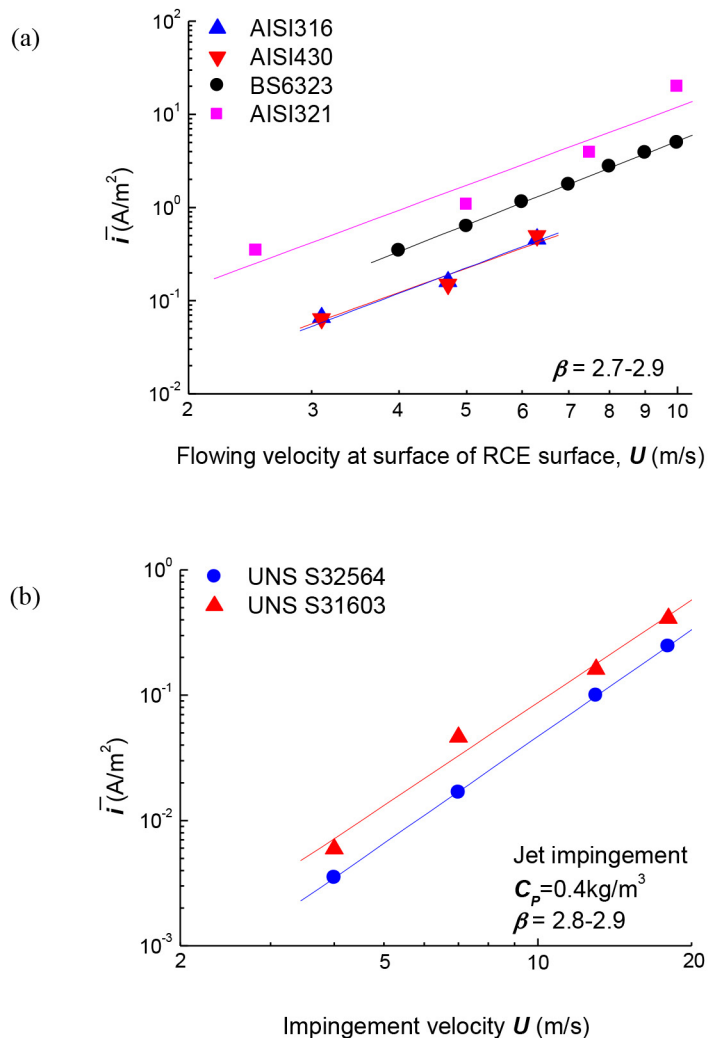


FIGURE 27: Dependence of Corrosion Current Densities on Flow Velocities of Slurries: (a) Rotating Cylinder Electrode (RCE) System and (b) Jet Impingement

⁽⁸⁾Health and Safety Executive (HSE), 2 Southwark Bridge, London SE1 9HS UK.

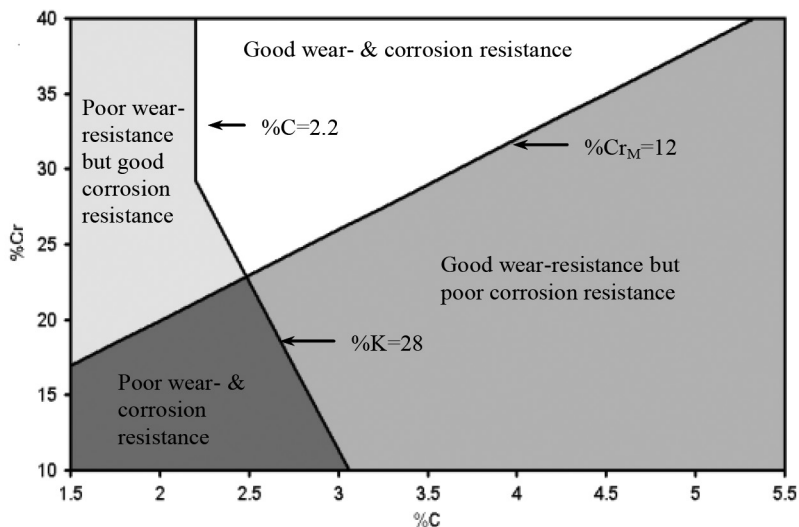


FIGURE 28: Wear/Corrosion Performance Map of Chrome White Irons (%C and %Cr are Weight Percentage of Carbon and Chromium in Materials, %Cr_M and %K are the Chromium Content in the Matrix and the Weight Percentage of Carbides in Chrome White Irons)

Erosion Resistant Coatings and Deposits

Erosion resistant coatings are effective, particularly on key items such as pump and valve internals. The CWIs and MMCs are the most commonly used coating materials. WC and W2C are almost as hard as diamond. They are particularly suitable to be used in hardfacing. Tungsten carbide overlay coatings are applied by high-velocity oxygen fuel spraying (HVOF) or welding. The coating thickness obtained by HVOF technique is between 10 to 1000 mm, which is suitable for valves, pistons, and pump impellers. The extremely abrasive conditions in oil drilling demand thicker coatings and better bonding. The plasma-transferred arc (PTA) process, using a multilayer deposition technique, produces facings up to 120 mm. It is widely used in oil extraction equipment in the oil sand industry.³³⁵ Other coating processes, involving chemical vapor deposition, have been used to produce ultra-hard coatings like diamond for pump components and mechanical seals.

Application of Inhibitors and Chemical Control

The addition of inhibitor efficiently reduces the corrosion and corrosion-enhanced erosion material loss. High concentrations of chromates and nitrites act as passivating inhibitors, whereas chromates at low concentrations act as cathodic inhibitor, and were used in the first long distance coal-slurry pipelines.^{336,337} However, chromates are highly toxic, so efforts have been made to find environmentally-friendly inhibitors. Non-chromate inhibitors used in the cooling water systems showed little benefit in erosive slurries when used alone or along with chromates. Schmitt et al. reported that the addition of surface active compounds, such as polyamineamide, efficiently reduce the wall shear stress and, therefore, improve the protective function of surface scale.

Solution conditioning involves raising the pH and/or deaeration. Both have been applied to long-distance slurry pipelines. An increase in pH promotes pitting because a thicker scale is likely to form.^{338,339} Deaeration is achieved by adding oxygen scavengers, such as bisulfite or hydrazine. These are used extensively with oil-well water injection systems.³⁴⁰

Engineering Aspects

The previous sections are based on observed industry practices for upstream oil and gas. However, the principles could be suitably applied in other petrochemical areas, such as midstream and downstream. Essentially, the guidelines are based on second principles (applied) rather than the first principles (fundamental) as presented in the early text. This step change is often used in practice to allow fit-for-purpose solutions to be identified. The data is often then revised as the more fundamental and experimental data and equations are verified by subsequent testing, field extrapolations and project experience. The volume of work being done by Joint Industry Projects and the oil industry majors is prodigious, and as such this review is an insight, though an attempt has been made to focus on relatively recent developments and practices evolving mainly over the past several years, post 2000. The section draws, where possible, on a variety of standards, standard practices, and technical papers as well as actual relatively recent industry experiences via projects and as such is sometimes used as a preliminary guidance document. Erosion corrosion is still a major threat to offshore and subsea assets, with related failures being thought to account for more than 30% of all internal degradation-related hydrocarbon releases, or loss of containment.³⁴¹

As a result of many recent high profile erosion linked failures, there has been an increased impetus to examine such phenomena, and most of the engineering societies have shown much interest in furthering this agenda. Governing regulations have also played a critical role in driving these knowledge based initiatives. This paper therefore attempts to give some pragmatic guidance in this vast area of development. And to that effect some pertinent rules of thumb, observations, and caveats taken from best perceived engineering practices are in order and listed below. These are generally used as screening notes only, with careful interpretation used for each specific case in question, and always in consultation with the client materials and corrosion specialist. Where appropriate, guiding key performance indicators (KPIs) are typically suggested.

Since the mechanisms of corrosion and erosion acting together are very intricate and multifaceted, engineers often resort to a 'first pass' methodology of establishing corrosion rates and derived corrosion allowance (CA), and thereafter using an additive assessment for the erosion parameter. Useful guidance on the concept of CA is obtained from many sources. If the corrosion rate is worked out from historical data or from modeling studies (for example through commercially available models or the publicly available freeware such as NO or CA) then an adjudged allowance for erosion is made (usually in consensus with the client)^{342,343}.

The models only give general or uniform corrosion rates, and that the real value in corrosion modeling is not so much the absolute values, but the trends and changes. The use of more than one model allows for cross checking, where any three of the freeware models (NO, and CA) are used at a minimum and other commercial models if available. In cases of major conflict or disagreement, it is common to use the worst case corrosion/thinning values for best conservatism. There are many corrosion and erosion models commercially available (possibly > 15); if these are accessible they are usually explored. However, many similar software packages are often on hand in-house as spreadsheets or issued by certain companies for project specific analyses.³⁴⁴ Either way, the real value of corrosion and erosion modeling is mostly in helping the decision making process regarding materials selection and the differentiation between the use of carbon steel or the alternate CRAs.

Guidelines and Caveats

1. For carbon steel, for low risk erosion rate scenarios this is quantified at KPI values of 0.05 or 0.1 mm/y. If medium or high risks of erosion are present then more advanced analyses as available from independent testing. In practice such values could be up to and well in excess of 10 mm/y. Therein sits the predicament, namely what data to use to support one's design rationale. The subject is ever complex and such decision making often has to rely on the planned design economics and the project costs entailed capital expenditure (CAPEX) versus operating expenditure (OPEX). The solutions commonly fit for the life cycle targeted, and typically either use thicker steel (greater corrosion allowances) or stipulate the use of a more CRA; the latter is solid pipe or steel pipe lined or clad with CRA, typically at 3 to 4 mm thickness, noting that less than 3 mm is generally not used because of possible mechanical wrinkling effects that would impact the integrity of the liner. The following sections delve into the governing criteria and guidelines considered applicable to flow enhanced corrosion, impingement, and erosion mechanisms.
2. The effects of flow are often treated as a separate individual mechanism, but the parameters affect other mechanisms, often in a subtle manner. This intermingled role can lead to significant localized corrosion. In reality, erosion is synergistic in an undefined relationship and therefore a major factor within the design discipline and more so with subsea flowlines where direct corrosion monitoring, re-engineering, or remedial action or retrofit are very difficult, very expensive, or often virtually impossible, thus putting even greater onus on design teams to get it right the first time.
3. Once flow is deemed to be an influential parameter, the engineers first pass visit is usually to the API RP 14E, through the concept of the committee consensus based C-factor, a means to quantify erosion. If the standard practice stipulates in practice a high C factor (150 to 200 or > 200) to give more latitude with production rates, then that increases the threat of erosion. Conversely, if lower C values are interpreted, typically say 80 to 100, then that is used to minimize the erosion threat by applying more conservatism. In cases of uncertainty, a C value of 100 is usually used at first iteration. The API approach alone is therefore misleading, but has much value if used with other trending and flow assurance data. Many companies have their own erosion guidelines, which are governing. As a rule, it is found that the API 14E is over conservative for liquid flows, but is sometimes under conservative for gas flows. Multiphase flowlines therefore lie somewhere in between. However, it is reasonably established that for inert non-corrosive gases, maximum flow velocities are on the order of 60 m/s. In contrast, the figure for liquids or multiphase flows is 20 m/s. However, once sand or particulates are introduced, the threshold values drop drastically. Results in that area are held by the JIP ventures. The data from the various JIPs are private for member company use only, and not published, hence the argument for the engineering design companies to get involved.
4. Oil and engineering design companies often use C factors, depending on the material as below:
 - a. Carbon steel: < 135
 - b. Stainless steel: ~135 to 200
 - c. Duplex stainless steels: > 200
 - d. Other CRAs (UNS N06625, UNS N08825, etc.): > 250
5. These values are guidelines for liquids with negligible sand/particulates. Different C-factors are usually used where specific application studies have suggested other more appropriate values. In all cases, frequent inspection and erosion survey data are used to verify continued fitness for service over the life cycle.
6. It is vital to take cognizance of all combined corrosion threats and to ensure sand or particulate controlling measures. Such particulate sizes and concentrations are critical since fine sands (< 10 μm and at concentrations up to 50 ppm) tends to absorb any inhibitor filming that is assumed, subsequently depleting the inhibitor species. Conversely, larger sizes and concentrations (> 100 μm , and > 1,000 ppm) are more dangerous, this is thought to be largely because the magnitudes are comparable to the boundary layer thicknesses, and are therefore expected to disturb the hydrodynamic boundary layer equilibria, and therefore also the 'passive' films, even if only episodic in nature. It is noted that for most fluids in motion and under a heat transfer, there is also a mass transfer (diffusion) boundary layer, and also a thermal boundary layer effect, depending on the temperatures involved and the heat flux in

play. As a rule, these tend to be at least an order of magnitude less than the hydrodynamic boundary layer thickness. Thus the importance of the size of sand particulates on a relative basis, hence we itemize as follows:

- a. Hydrodynamic boundary layer thickness: Typically 500 to 1,000 μm
 - b. Thermal boundary layer thickness: Typically < 50 to 100 μm
 - c. Diffusion boundary layer thickness: Typically 10 to 40 μm
7. Depending on the actual pressures and temperatures, other related phenomena such as cavitation are also a possible threat, particularly where gas bubbles are entrained and subject to bubble impingement and collapse under pressure fluctuations. Such mechanisms also hamper the efficiency of filming inhibitors by breaking protective films. It has been calculated that this gives rise to extremely high local pressures (up to 1 GN/m²). This exceeds the yield strength of most engineering materials and is thus capable of exerting severe surface damage. The impact is often seen with choke assemblies, at or downstream of sharp flow line geometry changes, with pump impellers, etc., especially when the equipment is operated outside its intended design characteristics. Some examples of choke internal sleeve materials such as the 13% martensitic stainless steels and the tungsten carbide alloys being destroyed by the combination effects of erosion, sand and cavitation within short periods (days and weeks) have been observed.
8. As a rule, flow related corrosion activity is highly dependent on the flow regime present. There are many flow regimes defined as described earlier, see Figure 19 as an illustrative example. In principle, for oil and gas liquid dominated flowlines, we define the extent of turbulence by the following criteria based on the Reynolds number (Re):
- a. Laminar flows Re: < 2,000 to 2,500
 - b. Transitional flows Re: ~ 2,300 to 3,000
 - c. Turbulent flow > Re: 2,500 (normally industry Re ~ 20,000 to 50,000)
 - d. Highly turbulent flows > 100,000
9. Most of the time, pipeline flows are turbulent, but it is known that mini-stagnant zones can exist within the steady turbulent envelope, leading to accelerated secondary corrosion, often stimulated by other mechanisms often not normally associated with flow, such as MIC. These mini-stagnant areas are often found downstream of horizontal flowline girth welds, at changes in direction (tees, wyes, etc.), and other bottom of line (BOL) positions such as low topography. If the threat of such localized erosion or significant induced stagnant pocket corrosion is determined to be high/severe, then remedial options such as the discrete use of internal coatings such as locally applied marine, epoxy or thermal spray aluminum (TSA) is considered. Note: With all such solutions, one typically develops on line monitoring to assure ongoing solution verification and integrity of the parts affected.
10. MIC, although a self-standing threat, has also been seen as a major flow related threat and potentially hazardous mechanism, either under stagnating or low flow laminar flow regimes, with serious failure consequences. The mechanism is not often associated with high flow turbulent regimes, and is therefore often missed. The key factor is whether or not the presenting biofilming or sulfate reducing bacteria (SRB) activity can find a shielded habitat. Quite often, these bacteria, if they are present in the system, can settle out at crevicing or mini stagnant zones, even under nominally high turbulent flow regimes. Once such colonies are created, proliferation sometimes occurs. If this happens, then other secondary effects can take over, leading to corrosion failure. Some examples involve low levels of planktonic bacteria remaining entrained in highly turbulent flows but being subject to increased concentration at re-deposited zones in sheltered areas (sessile activity). Such MIC activity can enter the fray unexpectedly, often at vulnerable periods, entering the corrosion reaction sequence and then disappearing without trace, as fully turbulent flows are re-established to sweep off the biofilms, often leaving only signs of the microbial history. To address this critical parameter, chemical vendor companies are tasked to maintain the following KPIs, even under fully turbulent flows, by appropriate biocidal control:
- a. Planktonic bacteria < 1 to 10 colonies/ml
 - b. Sessile colonies < 1 to 10 colonies/cm²

It is clear that flow-assisted corrosion and erosion phenomena are often associated with other accelerated corrosion activity. For example via direct sweet (CO₂) corrosion activity which also occurs under upset, excursions, or stagnating flows, often at magnetite (Fe₃O₄), siderite (FeCO₃) or iron sulfide (FeS) embedded scales, with subsequent 'galvanic' action at any spalled scales next to bare steel. The attack morphology is often recognized as a 'mesa' type pitting attack, and is often driven by the effects of enhanced sweet and dissolved oxygen mass transport mechanisms. It is also now clear that the presence of sand and particulates under certain circumstances accelerate corrosion activity, even under nominally well inhibited regimes. Much research is being done in these areas, and it is found evidently that provided the correct inhibitor formulations are used and sufficient increases in inhibitor dose are applied in a timely manner, then satisfactory corrosion inhibition is resumed.

There are no rules regarding localized corrosion and erosion, but it is certain that prevention is better than the cure. Hence, the engineer's objectives are to address these threats from early concept design through detail design and on to installation and operations. This includes the elimination of any pre-corrosion that could have started during storage or poor preservation. Such corrosion inevitably roughens up the surfaces, increasing friction factor, thereby leading to more disturbed fluid boundary layers, which promote erosion type mechanisms; smooth surfaces are usually better. Pre-corrosion also acts as an accelerator for flow assurance related scales such as waxes/hydrates/sulfates/carbonates, etc. Scales well anchored in this way invariably prove to be harder to remove. Damaging pre-corrosion typically occurs under various mostly preventable scenarios, typically:

- Poor storage conditions, prior to installation.
- Improper hydrotest exposures (contaminated fluid retention).
- Poor protection at commissioning (inadequate temporary preservation or inhibition).
- Pre-corrosion is often overlooked and is rarely treated as a critical variable impacting flow related corrosion phenomena, so suitable steps are desired to eliminate the threat.

Within the flow regime, surface wettability is also a major parameter, especially in tandem with corrosive species such as CO₂, water, chlorides, etc. The competition between oil and water wetting plays the deciding role. Generally, oil wetting is inhibitive, whereas water wetting is a root cause of flow assisted corrosion. The two wetting regimes have varying resistance to fluid shear, electrochemical (ions and polarity), and surface tension properties. The onset of corrosion has been linked to proportionality of the two (e.g., water cut ~1 to 30%), with most onerous conditions being at > 10%, but corrosion has also been observed at low values. There are no clear thresholds, but properties such as light/heavy, API gravity, contaminants, stickability, etc. are likely rate-controlling.

As with other localized corrosion phenomena, the most difficult prediction is not so much whether localized corrosion occurs, but more likely the question is invariably where. That is typically a function of water wetted zones flow regimes and the setting up of localized corrosion cells. Internal corrosion direct assessment methods are currently being developed to determine the main water wetting sites within a pipeline as the topography and angle of inclination varies.³⁴⁵ Flow related phenomena and erosion are usually responsible for localized corrosion activity, particularly if unsteady and transient flow regimes exist. Under such circumstances, corrosion activity is likely to be initiated at such excursions, and propagated at steady more uniform flow regimes. The engineer commonly also watches out for significantly changing or fluctuating flow regimes within the design envelope, including changes in reservoir water content chemistry, to ascertain the scaling (protective) or non-scaling (corrosive) tendency of the waters, thereby allowing better chemical dosing adjustments to be made.

Much research in pertinent areas concerning erosion and the interface with corrosion, hydraulics, and inhibition is underway, and it is relevant to stipulate that most of this is being done at the main R&D centers around the world, most often in collaboration with industry experts and specialists. Other purely industry-based standards have also evolved more on the materials selection side, either as private company documents or as public guidelines, driven by the not-for-profit engineering societies. The latter invariably provide numerous KPI type guidance regarding acceptable material solutions, including when to revert to the CRAs, and useful definitions of corrosion, erosion, cracking, and other failure modes. In particular, the various JIPs underway are thought to be generating a great deal of useful practical data for use in predicting corrosion and erosion rates for many offshore or subsea design scenarios. The data is experimental, but is continually being revised and updated for valuable use of the member companies. At the same time, significant R&D, as well as experience-based data is being compiled, such that significant advances and confidence in tackling erosion-corrosion issues are being noted.

Corrosion and Erosion Allowance: The Paradox

The two extremes of simplicity and combined complexity of the Corrosion Allowance (CA) concept is often seen as a paradox, but is addressed if we assume at 'first pass' that all mechanisms are additive by a suitable judgment of Equation (83):

$$\text{"Total CA = Uniform CA + Erosion Allowance + Pitting Allowance + Crevice Rate, etc."} \quad (83)$$

This approach is useful provided the localized corrosion evaluations are based on reasonable assumptions and sensible values are used for the case in question. In contrast, the more complex cases of inter-mechanistic synergism (or indeed antagonism) are addressed by current JIPs.

If we accept that most CO₂ corrosion models are based on the updated De Waard Milliams approach with flow sensitivity, and essentially assume single phase water wetting with dissolved CO₂ (no oxygen) for carbon steel dissolution, then we progress as follows in Equation (84):

$$\text{Log (Vr)} = 4.93 - 1119/T + 0.58\text{log (pCO}_2\text{)} - 0.34 (\text{pHact} - \text{pHCO}_2) \quad (84)$$

Where:

$$V_m = 2.45 U^{0.8} / d^{0.2} (pCO_2)$$

$$1/V_{cor} = 1/V_r + 1/V_m$$

V_r and V_m are kinetic and mass transfer reaction rates

Once V_r and V_m are estimated, the corrosion rate (V_{cor}) is calculated and cross checked with other correlations and practical field data.

The important realization is that early work by De Waard and Milliams did not recognize flow as an influential parameter. The later equations and subsequent HSE and DNV correlations have emphasized such influence, albeit on an applied empirical basis. It is therefore important to take best account of these parameters at a detailed design level to specifically quantify such localized corrosion and erosion phenomena on a feature by feature basis. Once these are accurately defined, the selection of inhibitors and control of flow regimes are better rationalized.

To that effect, the relevant enabling correlations appear to be of the form often known as the Dittus Boelter or Sader Tate type relationships, as shown in Equations (85) and (86):

$$Sh \approx 0.023 Re^{0.8} Sc^{0.30} \quad (85)$$

Where:

Sh = Sherwood number

Re = Reynolds number

Sc = Schmidt number

And:

$$Nu \approx 0.023 Re^{0.8} Pr^{0.3} \quad (86)$$

Where:

Nu = Nusselt number

Pr = Prandtl Number

These correlations are subsequently used through the Chilton Colburn or Reynolds type analogies to link corrosion, heat transfer, and flowline hydraulic coefficients in a meaningful manner. Many examples exist, and the reader is referred to the publications by DNV and the UK HSE as well as API to help quantify erosion patterns at critical geometries.³⁴⁶ For example, for high risk flowline welds, the erosion rate immediately downstream of a weld (probably worst case threat) is estimated for steel by Equation (87):

$$ER \approx 3.3 \cdot 10^{-2} \cdot (7.5 \cdot 10^{-4} + h) \cdot U_p^{2.6} \cdot D^{-2} \cdot m.p \quad (87)$$

Where:

ER = Erosion Rate

D = Internal Diameter

H = height of weld

$m.p$ = mass flow sand

U_p = sand impact velocity (approximating to fluid velocity)

All inputs are in SI units to cover for the constants. A more detailed appraisal is not appropriate at this stage for all geometries, but suffice it to say that similar correlations are applicable for other important features such as straights, bends, reducers, tees, etc. The formulae for straight sections and bends tend to contain geometrical constants, which are selected from data for various geometries. That is explored further at equipment detail design once data per equipment dimensions and actual flow regime descriptions (oil, gas, water dominated, fully turbulent, laminar, transitional, etc.) are more firmly established. Other work by the oil companies has added much value to the existing API/NACE standards and led to the use of more fine-tuned correlations for erosion prediction and online monitoring.

Inherently Safe Design

The technical challenge from an engineering perspective is to accept that corrosion initiation often occurs under non-steady conditions, while propagation thereof is often under steady state operation. In practice, such problems at excursions lead to conflict between the codes, inaccurate prediction of erosion/corrosion, accelerated damage chokes, bends, jumpers, discontinuities,

etc. Some of these difficult, but definable trends are addressed via interrogation of commercially available computational fluid dynamic (CFD) modeling such as the various flow assurance OG type modeling. There are promising solution options with internal coatings/clad/liners, but care is typically taken to alleviate changes in local surface polarization at undercut sites, localized eddies, and temperature gradients, etc. Nevertheless, reliable corrosion and erosion monitoring techniques such as intrusive (probes and coupons) and non-intrusive (acoustic transducers), field signature methods (FSM), guided wave ultrasonics, wall thickness mapping, thermal imaging, etc. are proving to be very good early warning systems for high risk components etc. The close synergy between flow assurance and corrosion integrity teams is now more apparent, and many companies are now quite successfully amalgamating such groups, obtaining significant technical advantage

From a mechanical integrity perspective, it is very important for engineers to think carefully beyond the immediate design codes of practice, since corrosion and degradation begin fairly soon after start up, often with major degradation issues and problems with continued operability or fitness for service. To that effect, engineers generally consider using the principles of inherently safe design (ISD) to build in sufficient conservatism and safety. Some important definitions as part of broad integrity management programs are described as follows:

- Hazards—Materials degradation, loss of mechanical properties, or corrosion are considered a hazard. Thus legitimizing the risk-based analyses defined as: $\text{Risk} = \text{Probability of Failure} \times \text{Consequences}$.
- Keeping material and corrosion failures 'As Low As Reasonably Practicable' (ALARP). This provides the defensible criteria basis for public and environmental concerns, subsequently reducing the important financial incentives to a less dominant overriding parameter.
- Inherently Safe Design (ISD) designing such that material and corrosion failures are avoided or reduced to acceptable levels, design to ALARP means 'fail safe' or 'safe life' depending on objectives. In practice, this usually means fewer moving parts, greater emphasis on reliability, and the use of CRAs, with attention to all corrosion threats under all service or non-service conditions.

ALARP and ISD have the potential to be accepted legal terms in a court of law. Both are strict, but typically enforce better dialogue, greater accountability, more lateral thinking, and ultimately promote safer life cycle, and transparent, solutions. If applied diligently, one offsets CAPEX with reduced OPEX.

From a predictive erosion perspective, it is common to allow for total wall thinning as a result of corrosion and erosion type degradation mechanisms. Generally, if this calculation shows a total CA value of $CA > 10$ mm, then intervention via moving toward a suitably selected CRA material either as a solid material or as a lining or cladding option is often considered. Some operators and designers put this threshold at 8mm. Either way the final decision is based on the economics of the project and the cost implications both at CAPEX and OPEX stages of the project. Another major factor is the length of the pipeline. Generally speaking, pipelines beyond 15 km length tends to look more closely at carbon steel with highly diligent and aggressive first-in-class chemical inhibition typically with $> 97\%$ efficiency and $> 97\%$ availability. Internal coating options are also feasible, but would likely still use parallel inhibition schemes to cover for the protection of damaged coating sites. The inhibitors in that case would be highly proficient at addressing such sites under crevice corrosion conditions. Designers usually engage the services of experienced chemical vendors in this subject matter. The most frequently used alternative CRA material choices tend to be the nickel alloys, UNS N06625 and UNS N08825, with the martensitic and austenitic stainless steels also commonly used (typically 13% Cr and UNS S31600). Most projects these days are often schedule driven, meaning that fast but detailed advice is sought through guidelines from many sources, societies (NACE, API, ISO, etc.), and the various JIPs, industrial and academic sources now available.

Summary

It remains challenging to evaluate the erosion corrosion wastage of engineering materials and/or components in a quantitative way, because of the complexity resulting from synergisms among the factors relating to mechanics, chemistry and materials. The economic loss because of erosion corrosion is minimized by utilizing proper design, material selection, and chemical control.

This section provides the fundamental principles for better erosion understanding, and the pragmatic guidelines for better control based on best industry practices. The subject is a live work in progress with new data, new approaches, and new resolutions continually being offered and deployed.

For most cases in the absence of a full suite of data, the modern day methods of risk based mechanical integrity management provide one proven way for rapid growth. These methods engage a formalized sequence of design appraisal, erosion event history analysis, prioritized inspection planning, inspection activity, real time corrosion and erosion integrity analyses, mitigation and control. Some guidance in these areas has been provided.

By applying ISD principles in tandem with best industry practices to aggressive (high CO_2) corrosion and erosion conditions, one targets safer designs. By using simplified designs, more creative inspection, less maintenance, and less manpower to help better meet

the life cycle objectives, life cycle integrity and fitness for service is achieved. In this context, setting the goals is paramount; for example, identifying the hazards and designing out the problem areas is best done by multi-disciplined project groups in small step sequences. The methodology is a difficult change in thinking, but serious traction as a paradigm shift has been noted when it has been applied. The main advantage of this process is that it eliminates the erroneous thinking that compliance with codes is all that is used in practice. Corrosion and erosion phenomena are major areas of weakness within failure mode and effects, understanding, and control. However, modern modeling and inherently safer design techniques and JIP-driven corrosion management programs are pushing the solutions base in the right direction. It is advantageous for the engineering companies to stay abreast of such safety critical findings and to participate in such leading edge activities.

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Appendix A: Acronyms for Models

This appendix is intended to provide supplementary information only, although it may contain mandatory or recommending language in specifications or procedures that are included as examples of those that have been used successfully. Nothing in this appendix shall be construed as a requirement or recommendation with regard to any future application of this technology.

Model	Acronym
De Waard ^b	DW
NORSOK	NO
Hydrocor ^c	HY
Cassandra ^d	CA
Corplus ^e	CO
KSC ^f	KS
Multicorp ^g	MU
Freecorp ^h	FC
Electronic Corrosion Engineer (ECE) ⁱ	EC
Predict ^j	PR
SPPS_CO ₂ ^k	SP
UL Lafayette Corrosion Model (ULL) ^l	UL
OLI ^m	OL
University of Toronto/Southwest Research Institute (UT/SwRI) ⁿ	SR
CorPos ^o	CP
enpICDA ^p	EN
Sweetcor ^q	SW
Integrated Flow Internal Localized, MIC, and Solid ^r	IF
CheckWorks	CW
OLGA ^s	OG
Lipucor ^t	LP
Cormed ^u	CM
Dream ^v	DR
^b Software product of Shell International ^c Software product of Shell International ^d Software product of BP ^e Software product of TOTAL-Elf Aquitaine ^f Software product of Institute for Energy Technology ^g Software product of Center of Multiphase Technology, Ohio University ^h Software product of Center of Multiphase Technology, Ohio University ⁱ Software product of Intetech ^j Software product of InterCorr International, Inc. (now Honeywell Process Solutions) ^k Software product of University of Tulsa ^l Software product of University of Louisiana at Lafayette ^m Software product of OLI Systems ⁿ Software product of University of Toronto/Southwest Research Institute ^o Software product of Force Technology ^t Software product of Broadsword ^u Software product of Shell International ^v Software Product of CorrMagnet Consulting Inc./Interlace India Pvt. Ltd	

Appendix B:

Important Factors in CO₂ Corrosion Prediction Models

This appendix is intended to provide supplementary information only, although it may contain mandatory or recommending language in specifications or procedures that are included as examples of those that have been used successfully. Nothing in this appendix shall be construed as a requirement or recommendation with regard to any future application of this technology.

Table B1
Important Factors in CO₂ Corrosion Prediction Models

Model	DW	NO	HY	CA	CO	KS	MU	FC	EC	PR	SP	UL	OL	SR	CP	EN	SW	IF
Lab data, Field data model, Mechanistic model	L	L	M	L	F	M	M	-	L	L	M	F	M	-	L	-	L	L,F
Scale effect formation water*	N	M	N	W	W	M	M	-	W	S	S		W	-	M	-	W	S
Scale effect condensed water*	W	M	W	W	W	M	M	-	W	S	S		M	-	M	-	W	W
Effect of pH on corrosion rate*	W	M	W	W	M	M	M	-	W	S	S	S	W	-	M	-	W	M
Risk for localized attack	-	-	-	-	Y	Y		-	-	Y	-	Y	-	-	-	-	-	Y
Oil wetting effect crude oil*	S	N	M	N	M	N	S	-	S	S	N	S	N	-	M	-	N	S
Oil wetting effect condensate*	N	N	N	N	M	N	M	-	M	M	N	S	N	-	M	-	N	S
CaCO ₃ correction for pH	-	-	-	-	Y	-	Y	-	-	-	-	-	Y	-	-	-	-	Y
Effect of organic acid on corrosion	-	-	Y	Y	Y	-	Y	-	Y	Y	-	Y	-	-	-	-	-	N
Top of line corrosion	Y	-	Y	-	-	-	Y	-	Y	-	-	Y	-	-	-	-	-	N
Effect of H ₂ S on corrosion rate*	N	N	W	N	N	N	M	-	S	S	N	W	S	-	N	-	N	S
Multiphase flow calculation**	N	P	M	N	P	N	P	-	M	P	P	M	N	-	M	-	N	M
Open, Commercial, Proprietary	O	O	P	O	O	O	P	-	C	C	P	P	C	-	P	-	P	C

Y = YES, N = NO, U = UNKNOWN

* S - strong effect, M - moderate effect, W - weak effect, N - no effect

** P - point calculation, M - multiphase profile calculation, N - no multiphase flow calculation

Appendix C: Description of Corrosion Models

This appendix is intended to provide supplementary information only, although it may contain mandatory or recommending language in specifications or procedures that are included as examples of those that have been used successfully. Nothing in this appendix shall be construed as a requirement or recommendation with regard to any future application of this technology.

Name: DW	Version (date): 1995
Availability: Available to the public	Source: available from literature (see references)
Description The model developed by De Waard and coworkers has for several years been the most widely used CO₂ corrosion model. The first version was published in 1975 and was based on dependence of temperature and pCO₂ only.¹ This version was based on small-scale lab experiments. The model has been revised several times since, when different correction factors have been added to the original equation. Correction factors for the effect of pH and corrosion product scale were included in 1991.² Some of the factors were adjusted in the 1993 version, where also the framework for a new model with effect of fluid velocity was proposed.³ In the 1995 version the effect of mass transport and fluid velocity is taken into account, and also the steel composition was considered.⁴ The 1995 version represents a best fit to a large number of corrosion flow loop data generated at Institute for Energy Technology (IFE).⁵ The model was developed primarily for wet gas pipelines. The model uses a scale factor to take account for corrosion product scales. The model was calibrated against laboratory data up to 80 to 90 °C (176 to 194 °F), and does not correctly account for formation of corrosion films above this temperature. The scale factor should be used only in absence of formation water. The model includes an on/off factor for oil wetting in crude oil systems, but does not apply to condensate. The model requires inputs in the form of CO₂ partial pressure, temperature, pH, liquid velocity and water cut. Other input is total pressure, hydraulic diameter, glycol concentration, oil type (crude oil or condensate) and water type (condensed water or formation water). The model includes pH calculation only for pure condensed water or condensed water saturated with corrosion products, and requires pH as a separate input when formation water chemistry is specified. However, because of the moderate account for protective films the model has relatively little sensitivity to variation in pH.	
Conditions of application: Does not address H ₂ S	Limits of application: n/a
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Name: CA	Version (date): 1997
Availability: Not available to the public, shelved ca. 2009. New version is not available to the public.	Source: n/a
Description The Cassandra model is BP's implementation of the De Waard model, including BP's experience in using this model.¹ The model is openly available. In this model, a pH calculation module is included, in which the pH value is calculated from the CO₂ content, temperature and full water chemistry. The effect of protective corrosion films is included or excluded by the user by choosing the scaling temperature. Above the scaling temperature, the corrosion rate is constant instead of reduced with increasing temperature as in the De Waard model. The model thereby gives less credit for protective films at high temperature than the De Waard model. Oil wetting effects are not included in this model. Although not covered in the model calculations, important aspects for practical use of this model is the inclusion of corrosion inhibitor availability rather than inhibitor efficiency and the use of corrosion categories as a way of quantifying the corrosion risk.² The model takes CO₂ mole %, temperature, total pressure, liquid velocity and water chemistry as major input parameters. Other input parameters include hydraulic diameter and glycol concentration, oil type (crude oil or condensate) and water type (condensed water or formation water). The model reports a corrosion rate which is the average of the values based on the De Waard 1993 and 1995 versions, but with the 1993 value as the minimum value: as the 1995 version is regarded as not accurate for low flow velocities. Acetate in the water analysis is assumed to be present as acetic acid, giving a lower pH value when acetate is present. The presence of acetic acid is pointed out as important because of both the effect of acetic acid on the corrosion rate and the possible overestimation of bicarbonate content and pH from a water analysis when acetate is present.³	
Conditions of application: Does not address H ₂ S	Limits of application: Information not available
References 1. A. J. McMahon, D. M. E. Paisley, "Corrosion Prediction Modelling - A Guide to the Use of Corrosion Prediction Models for Risk Assessment in Oil and Gas Production and Transportation Facilities," Report No. ESR.96.ER.066, (Sudbury, UK: BP International, 1997). 2. B. Hedges, D. Paisley, R. C. Woollam, "The Corrosion Inhibitor Availability Model," CORROSION/2000, paper no. 00034, (Houston, TX: NACE, 2000). 3. B. Hedges, L. McVeigh, "The Role of Acetate in CO ₂ Corrosion: the Double Whammy," CORROSION/99, paper no. 99021 (Houston, TX: NACE).	

Name: NO	Version (date): Rev 2 (2005)
Availability: Available to the public	Source: http://www.standard.no/petroleum
Description The empirical Norsok M-506 model is mainly based on laboratory data at low temperature and a combination of lab and field data at temperatures above 100 °C (212 °F).^{1,2} The model was developed by the Norwegian oil companies, and has been issued as a standard for the Norwegian oil industry. The model is fitted to much of the same IFE lab data as the De Waard 95 model, but includes in addition more recent experiments at 100 to 150 °C (212 to 302 °F), and takes larger account for the effect of protective corrosion films and therefore predicts lower corrosion rates at high temperature and high pH than the De Waard model.³ The model is considerably more sensitive to variation in pH than the De Waard model. The model does not account for any effect of oil wetting. The model takes temperature, total pressure, CO₂ content, pH, wall shear stress and glycol concentration as major input and contains modules for calculating pH and wall shear stress. Three options for calculating pH are available. For condensed water without corrosion products the pH is given by the temperature and CO₂ partial pressure. The pH in condensed water saturated with iron carbonate produced by corrosion can also be calculated. For formation water the pH calculation is based on a specified bicarbonate content and ionic strength from a water analysis. Wall shear stress is calculated from production rates and pipe diameter. The model is used for temperature 5 to 150 °C (41 to 302 °F), CO₂ partial pressure 10–1,000 kPa, pH 3.5–6.5 and wall shear stress 1–150 Pa. The model is not intended for corrosion prediction in systems where pH stabilization is used for corrosion control. The latest version of the model is Revision 2, issued in 2005. In this version the lower temperature limit for the model was extended from 20 to 5 °C (41 °F) and a lower limit of 0.1 bar CO₂ partial pressure was introduced.⁴	
Conditions of application: The model is not intended for corrosion prediction in systems where pH stabilization is used for corrosion control and does not address H₂S.	Limits of application: Temperature: 5 to 150 °C (41 to 302 °F), CO₂ partial pressure: 10–1000 kPa, pH: 3.5–6.5, and Wall shear stress: 1–150 Pa
References 1. A. M. K. Halvorsen, T. Søntvedt, "CO₂ Corrosion Model for Carbon Steel Including a Wall Shear Stress Model for Multiphase Flow and Limits for Production Rate to Avoid Mesa Attack," CORROSION/99, paper no. 99042 (Houston, TX: NACE, 1999). 2. "CO₂ Corrosion Rate Calculation Model, Rev. 2," NORSOK standard No. M-506, http://www.standard.no/petroleum, (Oslo: Standards Norway, 2005). 3. A. Dugstad, L. Lunde, K. Videm, "Parametric Study of CO₂ Corrosion of Carbon Steel," CORROSION/94, paper no. 94014 (Houston, TX: NACE, 1994). 4. Stein Olsen, Anne Marie Halvorsen, Per G. Lunde, Rolf Nyborg: "CO₂ Corrosion Prediction Model - Basic Principles," CORROSION/2005, Paper no. 05551 (Houston, TX: NACE, 2005).	

Name: CO	Version (date): v.3.0 since 02/2009
Availability: Restricted public	Source: n/a
Description CO is a CO₂ and erosion-corrosion prediction tool developed in 2000 from a combination and improvement of two older tools (CM and LP). This model is based on a detailed analysis of the field experience of Total since the early 80s.¹⁻⁵ It predicts the fluid corrosiveness on wells, pipelines and process facilities in three or five categories (from “very low” to “very high”) depending on the level of available data. This model contains a complete pH/solubility calculation module that includes the effect of calcium and iron carbonate saturation. In addition to this module in house empirical criteria are used to determine this classification in categories. These criteria have been progressively developed from wide field experience and from intermediate calculated parameters. A “very high” corrosiveness indicates early failures have been reported in the field in less than 3–5 y, corresponding to corrosion rates in excess of 3 mm/y. A “very low” corrosiveness indicates there is good field experience without any corrosion indication after more than 30–40 y service life, i.e., corrosion rates less than 0.1 mm/y. Free acetic acid and pH are identified as key parameters for corrosion prediction. A corrosion decrease as a result of oil wetting is also calculated, although only as an indication. Erosion-corrosion evaluations are done with respect to liquid fluids, with no consideration of the erosive effect of solid particles. Calculations are done with reference to API-RP-14E, with C factors recommended from experience. Corrosion predictions from this model are limited to sweet fluids. No sour weight loss corrosion prediction criteria are presently included. On the other hand, a sour service module calculating the sour severity as per NACE MR0175/ISO 15156 document (i.e., vs. pH and H₂S partial pressure) is included for H₂S cracking assessment. Calculations are done in three possible conditions: with the given water analysis, with native condensed water and with condensed water saturated in corrosion products, e.g. to cover facilities where the amount of condensing water is very low.	
Conditions of application: Does not address H₂S	Limits of application: Information not available
References 1. M.R. Bonis, J.L. Crolet, “Basics of the Prediction of the Risks of CO₂ Corrosion in O&G Wells,” CORROSION/89, paper no. 89466 (Houston, TX: NACE, 1989). 2. J.L. Crolet, M.R. Bonis, “Prediction of the Risks of CO₂ Corrosion in O&G Wells,” <i>SPE Production Engineering</i> 6, 4 (1991): p. 449. 3. J.L. Crolet, N. Thevenot, A. Dugstad, “Role of Free Acetic Acid on the CO₂ Corrosion of Steels,” CORROSION/99, paper no. 99024 (Houston, TX: NACE, 1999). 4. Y.M. Gunaltun, “Combining Research and Field Data for Corrosion Rate Prediction,” CORROSION/96, paper no. 96027 (Houston, TX: NACE, 1996). 5. Y.M. Gunaltun, D. Larrey, “Correlation of Cases of Top of Line Corrosion with Calculated Water Condensation Rates,” CORROSION/2000, paper no. 00071 (Houston, TX: NACE, 2000).	

Name: HY	Version (date): 2002
Availability: Not available to the public	Source: N/A
Description The Hydrocor model has been developed by Shell to combine corrosion and fluid flow modeling and is Shell's preferred tool for CO₂ corrosion prediction in pipelines. Different CO₂ corrosion models are coupled to models for multiphase flow, pH calculation and iron carbonate precipitation.¹⁻³ This enables calculations of the corrosion rate over a pipeline profile. An oil wetting factor is used for crude oil systems, but not for gas condensate, which is not regarded as giving any protection by oil wetting. Oil wetting and no corrosion is assumed when the water cut is below 40 % and the liquid velocity is above 1.5 m/s. The scale factor is applied for condensed water cases, but not for formation water cases, as porous mixture scales may form with little protection. Prediction of top-of-line corrosion is also included as well as simplified models for H₂S corrosion and organic acid corrosion.⁴ The mechanistic CO₂ corrosion model LCR+ developed by Pots is used for the CO₂ corrosion prediction, while comparison with the De Waard model is also provided. The program includes a fluid flow model which calculates pressure, temperature and flow profiles along a pipeline. This is then used for predictions of corrosion rate along the pipeline. Main input parameters are inlet pressure and temperature, CO₂ and H₂S mole %, bicarbonate, organic acid and glycol content, pipe diameter and production rates. The program also asks whether there is formation water or condensed water and whether the oil is gas condensate or crude oil. It is also possible to use pipeline or well profile, gas molecular weight and oil density as input when available. The pH calculation takes account for production of iron and bicarbonate as a result of corrosion and to iron carbonate precipitation, giving an increase in pH along the pipeline. The model includes relatively small effects of protective corrosion films and has little sensitivity towards variation in pH. It is aimed at predicting on the conservative side in order to avoid predicting low corrosion rates for systems where failures may occur. An oil wetting factor is used when crude oil is present, but not for gas condensate, which is not regarded as giving any protection by oil wetting. Oil wetting and no corrosion is assumed when water cut is below 40% and liquid velocity is above 1.5 m/s.	
Conditions of application: n/a	Limits of application: n/a
References 1. B.F.M. Pots, "Mechanistic Models for the Prediction of CO₂ Corrosion Rates under Multi-Phase Flow Conditions," CORROSION/95, paper no. 95137 (Houston, TX: NACE, 1995). 2. E.W.J. van Hunnik, B.F.M. Pots, E. L. J. A. Hendriksen, "The formation of Protective FeCO₃ Corrosion Product Layers in CO₂ Corrosion," CORROSION/96, paper no. 96006 (Houston, TX: NACE, 1996). 3. B.F.M. Pots, R.C. John, I.J. Rippon, M.J.J.S. Thomas, S.D. Kapusta, M.M. Girgis, T. Whitham, "Improvements on De Waard-Milliams Corrosion Prediction and Applications to Corrosion Management," CORROSION/2002, paper no. 02235 (Houston, TX: NACE, 2002). 4. B. F. M. Pots, E. L. J. A. Hendriksen, "CO₂ Corrosion under Scaling Conditions - The Special Case of Top-of-Line Corrosion in Wet Gas Pipelines," CORROSION/2000, paper no. 00031 (Houston, TX: NACE, 2000).	

Name: KS	Version (date): Version 3.01, issued in 2004.
Availability: Public	Source: Obtained from Institute for Energy Technology.
Description The KSC Model is a mechanistic model for CO₂ corrosion with protective corrosion films developed at Institute for Energy Technology within the joint industry project Kjeller Sweet Corrosion V.¹ The model is based on an electrochemical model by building it together with a transport model.² The model simulates electrochemical reactions at the steel surface, chemical reactions in the liquid phase, diffusion of species to and from the bulk phase, diffusion through porous corrosion films and precipitation of iron carbonate in the corrosion film. The properties of the protective corrosion films are correlated with a large number of corrosion loop experiments. The model calculates the concentration profiles and fluxes of the different species and the resulting corrosion rate. The model calculates both a corrosion rate in the absence of protective films, a corrosion rate with protective corrosion films present and a risk for mesa attack. The corrosion rate with protective films is the preferred value, but when the risk for mesa attack is high the corrosion rate without film should be used. The model takes temperature, total pressure, CO₂ partial pressure, pH and liquid flow velocity as major input. The model contains a module for calculating pH with bicarbonate content and ionic strength as additional input. The model includes a relatively strong effect of protective corrosion films which is sensitive to pH and temperature, and therefore tends to predict low corrosion rates for high temperature and high pH. The model does not take any effect of oil wetting into account. The strength of the KSC model is primarily as a tool for understanding the different processes taking place during CO₂ corrosion of carbon steel in the presence of protective corrosion films. It is not primarily intended as a design tool.	
Conditions of application: n/a	Limits of application: Temperature: 5 to 150 °C (41 to 302 °F), CO₂ partial pressure: 10–2,000 kPa, and pH: 3.5-7
References 1. S. Netic, M. Nordsveen, R. Nyborg, A. Stangeland, "A Mechanistic Model for CO₂ Corrosion with Protective Iron Carbonate Films," CORROSION/2001, paper no. 01040 (Houston, TX: NACE International, 2001). 2. S. Netic, J. Postlethwaite, S. Olsen, "An Electrochemical Model for Prediction of Corrosion of Mild Steel in Aqueous Carbon Dioxide Solutions," <i>Corrosion</i> 52, 4 (1996): p. 280.	

Name: SP	Version (date): 2004-v2
Availability: Available to members of the JIP	Source: N/A
Description The CO₂ corrosion model for pipe flow conditions developed at the University of Tulsa is a mechanistic two-phase flow model for CO₂ corrosion of carbon steel piping with detailed modeling of the kinetics of electrochemical reactions and mass transfer.¹ Inputs to the program include CO₂ partial pressure, temperature, pipe size, superficial liquid velocity, liquid density, liquid viscosity, superficial gas velocity, gas density, gas viscosity, pH (or option to calculate pH from the water chemistry), concentrations of iron, bicarbonate, and carbonate. The model does not consider a wetting effect of an oil phase. The model predicts the flow pattern (single phase liquid, bubbly, slug, or annular) and computes mass transfer coefficients based on a mechanistic mass transfer model.² Piping geometries include straight pipes and elbows.³ A feature of the model is its ability to predict formation of iron carbonate scales and the corrosion protection that they provide.^{4,5} The model also indicates what the corrosion rate would be without the formation of iron carbonate scales if the scales are removed, for example, by erosion or tools. The current version of the program is SPPS_CO₂ 2 Phase 2004-v2. The computer program implementing the model is available only to members of the Erosion/Corrosion Research Center JIP at the University of Tulsa. The model is most useful for oil and gas well conditions for which formation of iron carbonate films may be a factor and for which oil wetting effects may be expected to be minimal. Accuracy of the model has been verified only to temperatures below 105 °C (221 °F).	
Conditions of application: Does not address H ₂ S, oil wetting	Limits of application: Max temp of 105 C° (221 °F)

References

1. E. Dayalan, G. Vani, J.R. Shadley, S.A. Shirazi, E.F. Rybicki, "Modeling CO₂ Corrosion of Carbon Steels in Pipe Flow," CORROSION/95, paper no. 95118 (Houston, TX: NACE, 1995).
2. E. Adsani, S.A. Shirazi, J.R. Shadley, E.F. Rybicki, "Mass Transfer and CO₂ Corrosion in Multiphase Flow," CORROSION/2002, paper no. 02492 (Houston, TX: NACE, 2002).
3. J. Wang, S.A. Shirazi, J.R. Shadley, E.F. Rybicki, E. Dayalan, "A Correlation for Mass Transfer Coefficients in Elbows," CORROSION/98, paper no. 98042 (Houston, TX: NACE, 1998).
4. E. Dayalan, F. de Moraes, J.R. Shadley, S.A. Shirazi, E.F. Rybicki, "CO₂ Corrosion Prediction in Pipe Flow under FeCO₃ Scale-Forming Conditions," CORROSION/98, paper no. 98051 (Houston, TX: NACE, 1998).
5. F.D. de Moraes, J.R. Shadley, J. Chen, E.F. Rybicki, "Characterization of CO₂ Corrosion Product Scales Related to Environmental Conditions," CORROSION/2000, paper no. 00030 (Houston, TX: NACE, 2000).

Name: PR	Version (date): 5.0
Availability: Commercial package	Source: www.honeywell.com/ps
Description The Predict model is developed and maintained by Honeywell International (formerly InterCorr International).¹⁻³ The basic part of the model for CO₂ corrosion is based on the De Waard model and proprietary laboratory data for H₂S corrosion which is updated using correction factors. An effective CO₂ partial pressure is calculated and used for corrosion rate prediction from the in-situ pH for CO₂ systems. The model is based on the utilization of first principles of chemistry for pH and scale prediction and incorporates laboratory data from Joint Industry Projects for correlating effects of wall shear stress.⁴ The model takes temperature, CO₂ and H₂S partial pressure and water content as major inputs. The pH value is either given as an input or calculated from the bicarbonate content and ionic strength or complete water chemistry. The model includes a flow modeling module for calculation of flow velocity and flow regime for two phase systems. For low gas/oil ratios the model uses the water cut as an input in order to predict oil or water wetting and distinguishes between persistent and not persistent oil types. Oil persistency is an input from the user. The model has the capability to account for phase behavior of water. For high gas/oil ratios the model uses the dew point or water flow rate as an input in order to calculate water condensation. The model has a very strong pH dependence on the corrosion rate. This tends to yield lower predicted corrosion rates when the pH is greater than 5. The model includes strong effects of oil wetting and protective corrosion films, and this tends to give lower corrosion rates for certain situations when compared to DW 95 or NO model. The model also incorporates corrosion rate prediction for seawater corrosion, effect of dissolved oxygen and chlorides. It also indicates a likelihood of pitting along with a general corrosion rate. The model results include a predicted corrosion rate profile along a pipe or tubing length and the model is designed to support analyses of complete piping systems.	
Conditions of application: n/a	Limits of application: Maximum temperature: 500 °F Maximum H₂S and CO₂ partial pressure: 1,000 psi
References 1. S. Srinivasan, R. D. Kane, "Prediction of Corrosivity of CO₂/H₂S Production Environments," CORROSION/96, paper no. 96011 (Houston, TX: NACE, 1996). 2. S. Srinivasan, S. Tebbal, "Critical Factors in Predicting CO₂/H₂S Corrosion in Multiphase Systems," CORROSION/98, paper no. 98038 (Houston, TX: NACE, 1998). 3. K. A. Sangita, S. Srinivasan, "An Analytical Model to Experimentally Emulate Flow Effects in Multiphase CO₂/H₂S Systems," CORROSION/2000, paper no. 00058 (Houston, TX: NACE, 2000). 4. K. Yap, S. Srinivasan, "Key Factors in Development of a CO₂/H₂S Corrosion Prediction Model for Multiphase Oil/Gas Production Systems," CORROSION/2010, paper no. 10374 (Houston, TX: NACE, 2010).	

Name: SW	Version (date): n/a
Availability: Not available to the public	Source: N/A
Description The prediction tool SweetCor was developed for analysis of CO₂ corrosion by managing a large database of corrosion data from laboratory experiments and field data.¹ The approach is to group data by ranges of temperature and CO₂ partial pressure or by the stable corrosion product. Statistical analysis of the grouped data is used to make correlations for predicting corrosion rates for specific conditions. Corrosion prediction can be done either by using these prediction correlations or by filtering the database for conditions close to the conditions of interest in terms of temperatures, CO₂ partial pressure, flow/no flow and inhibitor/no inhibitor. When the database is filtered to select the conditions of interest, temperature, CO₂ partial pressure, flowing or stagnant conditions and presence or absence of inhibitors is taken as major input. This method is essentially only sensitive to temperature and CO₂ partial pressure and does not consider the pH value at all. The corrosion rate resulting from this method is the average of the data points which satisfy the filtering criteria. When the prediction correlations are used the major input is temperature, total pressure, gas and liquid superficial velocities, pipe diameter, CO₂ mole % and water chemistry. The predicted corrosion rate and pH value is then calculated. The model includes only a weak effect of protective corrosion films and does not take any effect of oil wetting into account. The pH value is calculated assuming a bicarbonate content in the water corresponding to water saturated with corrosion products, but the predicted corrosion rate is very little dependent on pH.	
Conditions of application: n/a	Limits of application: n/a
References 1. R. C. John, K. G. Jordan, A. L. Young, S. D. Kapusta, W. T. Thompson, "SweetCor: An Information System for the Analysis of Corrosion of Steels by Water and Carbon Dioxide," CORROSION/98, Paper No. 98020 (Houston, TX: NACE, 1998).	

Name: CP	Version (date): n/a
Availability: Commercial	Source: N/A
Description Corpos is a tool where results from multiphase flow calculations are combined with water chemistry calculation and a point corrosion model in order to calculate pH and corrosion rate along a pipeline.^{1,2} The model is based on using input from an external fluid flow model combined with calculation of a probability of water wetting and calculation of pH. Bicarbonate produced by corrosion is accounted for in the pH calculation, giving an increase in the pH along the pipeline. The NO model is then used to calculate the corrosion rate in several points along the pipeline. A probability of water wetting is calculated depending on water cut, flow regime, local phase velocities and emulsion stability. This gives lower corrosion rates than the NORSOK model for pipelines with very low water cut. A probability of water wetting is calculated depending on water cut, flow regime, local phase velocity and emulsion stability.	
Conditions of application: n/a	Limits of application: n/a
References 1. P.O. Gartland, "Choosing the Right Positions for Corrosion Monitoring on Oil and Gas Pipelines," CORROSION/98, paper no. 98083 (Houston, TX: NACE, 1998). 2. P.O. Gartland, J.E. Salomonsen, "A Pipeline Integrity Management Strategy Based on Multiphase Fluid Flow," CORROSION/99, paper no. 99622 (Houston, TX: NACE, 1999).	

Name: UL	Version (date): n/a
Availability: Available to members of the JIP	Source: N/A
Description The ULL corrosion model consists of a package of programs developed for gas condensate wells by the University of Louisiana at Lafayette (ULL), formerly the University of Southwestern Louisiana (USL).¹⁻³ The model calculates temperature and pressure profiles, phase equilibria, flow rates and flow regime and then calculates the pH profile and predicts the corrosion rate profile along the well. The model puts much weight on calculating the flow regime and the location for condensation of water and hydrocarbons in the well. The main input parameters for the model is gas, condensate and water production rates, gas composition, condensate density, well depth, tubing diameter, bottomhole, wellhead and separator temperature and pressure and water chemistry. The model has a strong effect of oil wetting when hydrocarbon condensation occurs. It typically predicts oil wetting and no corrosion for the part of the tubing where hydrocarbon condensation occurs, and corrosion when only water condenses. Developed only for gas condensate wells, it shows a strong effect of oil wetting when condensation occurs. It typically predicts oil wetting and no corrosion for the part of the tubing where hydrocarbon condensation occurs and corrosion when only water condenses.	
Conditions of application: n/a	Limits of application: n/a
References 1. C.D. Adams, J.D. Garber, R.K. Singh, "Computer Modeling to Predict Corrosion Rates in Gas Condensate Wells Containing CO₂," CORROSION/96, paper no. 96031 (Houston, TX: NACE, 1996). 2. R.S. Perkins, C.S. Fang, J.D. Garber, R.K. Singh, "Predicting Tubing Life in Annular-Flow Gas Condensate Wells Containing Carbon Dioxide", <i>Corrosion</i> 52, 10 (1996): p. 801. 3. J.D. Garber, V. Polaki, C. Adams, N.R. Varanasi, "Modeling Corrosion Rates in Non-Annular Gas Condensate Wells Containing CO₂," CORROSION/98, paper no. 98053 (Houston, TX: NACE, 1998).	

Name: OL	Version (date): 3.1
Availability: Commercial package	Source: www.olisystems.com
Description The corrosion model developed by OLI Systems combines a thermodynamic model for the concentration of molecular and ionic species of aqueous systems with an electrochemical corrosion model and a model for formation and dissolution of iron carbonate or sulfide scales.^{1,2} The model is based on detailed mechanistic modeling of the phase behavior and the various chemical and electrochemical reactions. The model takes temperature, pressure, flow velocity and molar composition of the corrosive medium as input. Much weight is put on thermodynamic calculation of the phase equilibria and the concentration of the different species in the system. Protectiveness of corrosion films is modeled by assuming that the electrochemical reactions only occur on the parts of the steel surface not covered by corrosion films. The scale formation parameters have been calibrated against selected laboratory data. The model does not take any effect of oil wetting into account.	
Conditions of application: n/a	Limits of application: n/a
References 1. A. Anderko, R. D. Young, "Simulation of CO₂/H₂S Corrosion Using Thermodynamic and Electrochemical Models," CORROSION/99, paper no. 99031 (Houston, TX: NACE, 1999). 2. A. Anderko, "Simulation of FeCO₃/FeS Scale Formation Using Thermodynamic and Electrochemical Models," CORROSION/2000, paper no. 00102 (Houston, TX: NACE, 2000).	

Name: EC	Version (date): 4.0
Availability: Commercial package	Source: www.intetech.com
Description The ECE model is developed by Intetech Ltd. This model predicts corrosion rates of carbon steel flowlines and tubing in the presence of CO₂ and H₂S. The model is also applied for processing facility piping and equipment. The influences of dissolved corrosion products, H₂S, crude oil type, acetic acid and flow regime on CO₂ corrosion rate are predicted. Inhibition scenarios are also compared. The model includes calculation of pH, including the saturation of the environment with Fe⁺⁺ ions and the influence of water and oil distribution on the corrosion rate. The oil wetting factor is dependent on the water-cut, oil density, the liquid flow velocity and the inclination of the flow.¹ The results of the model include a graph of corrosion rate with depth or distance along the line; a value reported for the maximum corrosion rate; a graph of the risk of failure as a function of time; a graph of pH variation with distance and a series of output data related to fluid velocities, estimated flow rates, partial pressures of acid gases, an approximate indication of the likely flow regime at the output of the system and evaluation of sour service requirements and API RP 14E erosional velocity limit (when appropriate). The corrosion model has a theoretical basis with various adjustments which has been calibrated on studies in diverse field conditions. These have included many studies of sour pipelines and facilities (including intelligent pig and other inspection data) and several sweet and sour oil and gas fields comparison of tubing damage based on caliper logs. Some of these have been published. The oil wetting correlation is based on a compilation of tubing corrosion data from a light crude oil field.² The oil wetting factor is dependent on the oil density, the liquid flow velocity and the inclination of the flow. An emulsion breakpoint is calculated from the oil density. This can be 40 to 50% water cut for heavy crude oils and close to zero for light condensate. For water cuts lower than the emulsion breakpoint, the water is believed to be present as a water-in-oil emulsion, and the predicted corrosion is low, but not zero. For higher water cuts, oil wetting is predicted to give only limited protection, as water droplets are predicted to separate out until a continuous water phase is obtained at high water cuts or low flow velocities. The critical flow velocity for water dropout is taken as 1 m/s for horizontal flow and lower for inclined flow.	
Conditions of application: n/a	Limits of application: n/a
References 1. C. De Waard, L.M. Smith, B.D. Craig, "The Influence of Crude Oils on Well Tubing Corrosion Rates," CORROSION 2003, paper no. 03629 (Houston, TX: NACE, 2003). 2. L.M. Smith, C. De Waard "Corrosion Prediction and Materials Selection For Oil And Gas Producing Environments," CORROSION 2005, paper no. 05648 (Houston, TX: NACE, 2005).	

Name: SR	Version (date): n/a
Availability: n/a	Source: n/a
Description The CO₂ corrosion model, developed originally at the University of Toronto¹⁻⁵ and later expanded at Southwest Research Institute (SwRI), is applicable to predicting the rate of corrosion in oil and gas production (downhole) and transportation systems. When the model is applied to predict the external corrosion rate of onshore transportation pipelines, the effects of dissolved oxygen in soils and external cathodic protection are considered. This CO₂ corrosion model is mechanistic in nature while emphasizing the known controlling variables. This model has been verified by the authors with significant amount of experimental data for temperature up to 90 °C and CO₂ partial pressure up to 6 atm. Being mechanistic, this model can be used for conditions other than those of the model validation. This CO₂ corrosion model covers the following steps: CO₂ dissolution, hydration, and diffusion; carbonic acid dissociation, diffusion and, at the steel surface, electrochemical reduction; ionic transport and interactions, and formation of ferrous carbonate precipitate; hydrogen ion and water reductions and iron oxidation at the steel surface; for external corrosion, also oxygen diffusion and reduction, possible formation of ferrous hydroxide as a precipitate, and steel potential shift by external cathodic polarization. In this model, CO₂ hydration (a slow step in the CO₂ chain reactions) is specially treated together with the kinetic equations which are expressed in special forms. The potential-driven ionic migration term in the ionic transport equation was neglected since it is insignificant compared to diffusion in a system containing sufficient supporting ions. This leads to the result that the concentration of each solution species is expressed by the single concentration of hydrogen ion at the steel surface and all the equations are solved easily with the use of Newton-Raphson iteration method. With the techniques provided in the references, this model can be readily implemented. Like any other mechanistic models, this model has its limitations. Some physical parameters of the model, such as exchange current density, can be sensitive to the conditions to be modeled such as the surface roughness. When this or any other model is implemented, these factors are taken into account to reflect reality. This model in its current status does not consider the effects of other inorganic acids, such as acetic acid, or oil wetting.	
Conditions of application: n/a	Limits of application: n/a
References 1. F.M. Song, D.W. Kirk, D.E. Cormack, "A Comprehensive Model for Predicting CO₂ Corrosion in Oil and Gas Systems," CORROSION 2005, paper no. 05180 (Houston, TX: NACE, 2005). 2. F.M. Song, D.W. Kirk, J.W. Graydon, D.E. Cormack, "CO₂ Corrosion of Bare Steel under an Aqueous Boundary Layer," <i>Corrosion</i> 60, 8 (2004): p. 736. 3. F.M. Song, D.W. Kirk, J.W. Graydon, D.E. Cormack, "CO₂ Corrosion of Bare Steel under an Aqueous Boundary Layer with Oxygen," <i>Journal of The Electrochemical Society</i> 149, 11 (2002): p. B479. 4. F.M. Song, D.W. Kirk, J.W. Graydon, D.E. Cormack, "CO₂ Corrosion of Bare Steel under an Aqueous Boundary Layer with Oxygen and Cathodic Protection," <i>Corrosion</i> 60, 9 (2004): p. 845. 5. F.M. Song, D.W. Kirk, D.E. Cormack, "Determination of Precipitates for CO₂ Corrosion of Steel under an Aqueous Boundary Layer," <i>Journal of Corrosion Science and Engineering</i> 3, 24 (2004).	

Name: EN	Version (date): n/a
Availability: Commercial package	Source: http://www.enpicda.com/
Description The EN model is a mass transfer model capable of yielding a general corrosion rate for uninhibited corroding multiphase or two-phase pipeline systems, in which O₂, CO₂, and H₂S contribute to corrosion of carbon steel pipes. The flow model predicts the flow pattern, liquid holdup, pressure drop, temperature drop and friction losses, and it calculates the liquid and gas velocities. The model predicts where solid deposition locations are most likely to occur by calculating the solids depositional velocity of the material being accumulated. It predicts solids accumulation as a function of distance and elevation change over discrete distances, as dictated by global positioning system (GPS) interval data collected and input into the model. The model does not predict the cumulative amount of the material, nor does it attempt to predict the under deposit corrosion rate behavior at this time. The in-house model is currently in its fourth generation, using FORTRAN as its format. The second generation model is available to the public via the internet but is restricted to calculating corrosion rates and other parameters in sub-region intervals.	
Conditions of application: n/a	Limits of application: n/a

Name: MU	Version (date): 2004
Availability: Limited to members of the JIP	Source: http://www.corrosioncenter.ohiou.edu/
Description MULTICORP is a transient mechanistic CO₂ corrosion model capable of predicting the corrosion of mild steel under conditions related to upstream production of oil and gas. The model is under development at the Institute for Corrosion and Multiphase Technology (ICMT), Ohio University, Athens, OH, USA. This model has been extensively calibrated and verified from large-scale corrosion and multiphase flow laboratory experiments and field corrosion databases provided by the major oil and gas companies. This mechanistic corrosion model covers kinetics of electrochemical reactions at the steel surface, such as iron dissolution, hydrogen evolution, etc., dynamics of coupled transient transport of multiple species between the bulk solution and the steel surface kinetics of chemical reactions and growth of iron carbonate and iron sulfide scales. The model predicts the effects of key variables on internal pipeline corrosion: two and three-phase flow, temperature, CO₂ partial pressure, H₂S content, organic acids, pH and brine chemistry, steel type, inhibition by crude oil and/or corrosion inhibitors, and magnitude and morphology of localized attack. Besides providing immediate answers (e.g., the corrosion rate), it 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. Because of the strong theoretical background, the user can extrapolate the predictions outside the calibration domain with much more confidence than for any (semi) empirical model. An included multiphase flow model provides successful prediction of the flow regime and whether water wetting of the pipeline occurs. Current developments include implementation of localized corrosion model, development of batch processing models, and case based prediction from experimental and field data. The 2004 model includes effects of crude oil chemistry. Wettability is based on the model published by Cai20 and includes a phase inversion point prediction and the flow pattern determination.	
Conditions of application: n/a	Limits of application: Temperature: 1 to 100 °C (33 to 212 °F) CO₂ partial pressure: 0–2 MPa H₂S content: 0–1 MPa Organic acids: 0–10,000 ppm pH: 3–7

References

1. S. Nešić, S. Papavinasam, W. Sun "Kinetics of Iron Sulfide and Mixed Iron Sulfide/Carbonate Scale Precipitation in CO₂/H₂S Corrosion," CORROSION 2006, paper no. 06644 (Houston, TX: NACE, 2006).
2. S. Nešić, W. Sun "A Mechanistic Model of H₂S Corrosion of Mild Steel," CORROSION 2007, paper no. 07655 (Houston, TX: NACE, 2007).
3. B. Brown, C. Canto, V. Fajardo, S. Nešić "Effect of Organic Acids in CO₂ Corrosion," CORROSION/2007, paper no. 07319 (Houston, TX: NACE, 2007).

Name: FC	Version (date): 1.0
Availability: Available to the public	Source: http://www.corrosioncenter.ohiou.edu/freecorp
Description FC is a freely available, simple corrosion prediction model (based on De Waard's equation) developed for use by the corrosion research community^{1, 2}. The software is developed by scientists and programmers at Corrosion Center (Ohio University)^{3,4} using publicly available knowledge of oil pipeline corrosion and it is distributed under GPL (General Public License) for free use by researchers, practitioners, and students of corrosion phenomena. FC V1.0 is a simple corrosion model, strongly rooted in theory. Currently, this model is capable of predicting uniform corrosion of carbon steel in environments containing CO₂, acetic acid, oxygen, and/or H₂S. Iron carbonate film formation is simulated using an empirical correlation to improve the accuracy of corrosion rate prediction. Contributions to corrosion from various corrosion species can be calculated, which enables the exploration of dominant corrosion species in the corrosion process. Polarization curves can also be displayed. In cases of H₂S corrosion, film formation is calculated and concentration profile of H₂S across mass transfer layers on steel surface is also displayed. FE is a user friendly add-in which allows rapid corrosion prediction calculation and display of the dominant corrosion mechanism. The program determines the dominant mechanism and displays it in a graphical format.	
Conditions of application: n/a	Limits of application: n/a
References 1. C. De Waard, D. E. Milliams, "Predictive Model for CO₂ Corrosion Engineering in Wet Natural Gas Pipelines," <i>Corrosion</i> 31, 12 (1975): p. 976. 2. C. De Waard, U. Lotz, "Prediction of CO₂ Corrosion of Carbon Steel", CORROSION/93, paper no. 93069 (Houston, TX: NACE, 1993). 3. S. Nesic, H. Li, D. Sormaz, J. Huang, "A Free Open Source Mechanistic Model for Prediction of Mild Steel Corrosion," 17th International Corrosion Congress, Las Vegas, Nevada, October 6-10, 2008. 4. S. Nesic, H. Li, D. Sormaz, J. Huang "An Open Source Mechanistic Model For CO₂/H₂S Corrosion of Carbon Steel," CORROSION 2009, paper no. 09572 (Houston, TX: NACE, 2009).	

Name: IF	Version (date): 1.0 (issued in 2013)
Availability: Commercial Product	Source: spapavin@corrsmagnet.com
Description IF Version 1 predicts the localized internal pitting corrosion of carbon steel in both sour and sweet environments. This model was developed based on the experiments carried out in the laboratory at high pressure and high temperature as well as on the actual pit growth rates in six operating fields over a period of four years. The model is further validated by field data from operating production and transmission pipelines. The inputs required are pipe diameter; pipe wall thickness; and pipe inclination; production or flow rates of oil, water, gas, and solid; temperature; total pressure; partial pressures of H₂S and CO₂; concentrations of sulfur, sulfate, bicarbonate, and chloride; Langmuir saturation index (LSI); total dissolved salts (TDS); and total settleable salts (TSS). The inputs can be manually entered into the software or downloaded directly from a database. This model predicts growth of localized internal corrosion pits, influence of microbiologically influenced corrosion (MIC), statistical nature of the pitting corrosion, variation of the pitting corrosion rate as a function of time and of length of the pipeline, precision of the outputs, flow regimes of single and multiphase flows, wall shear stress, pH, and variation of pressure and temperature along the pipe length. The outputs are displayed in graphical form and can be exported into other database.	
Conditions of application: Does not address uniform (general) corrosion, erosion, and erosion-corrosion.	Limits of application: Temperature: 5 to 125 °C (41 to 257 °F) Total Pressure: 0 to 750 psi H₂S Partial Pressure: 0 to 50 CO₂ Partial Pressure: 0 to 100 Bicarbonate: 0 to 4,000 ppm Chloride: 0 to 120,000 ppm Flow velocity: 0 to 5 m/s
Bibliography Papavinasam, S., Doiron, A. and Revie, R.W., Sizov, V. "A Model to Predict Internal Pitting Corrosion of Oil and Gas Pipelines." CORROSION 2007, paper no. 07658. Houston, TX: NACE, 2007. Papavinasam, S., Doiron, A., Panneerselvam, T., and R.W. Revie. "Effect of Hydrocarbons on the Internal Corrosion of Oil and Gas Pipelines." <i>Corrosion</i> 63, 7 (2007): p. 704. Papavinasam, S., Demoz, A., Michaelian, K., and Revie, R.W. "Further Validation of Internal Pitting Corrosion Model", CORROSION/2008, paper no. 08542. Houston, TX: NACE, 2008. Papavinasam, S., Doiron, A., and Revie, R.W. "Effect of Surface Layers on the Initiation of Internal Pitting Corrosion in Oil and Gas Pipelines." <i>Corrosion</i> 65, 10 (2009): p. 663. Demoz, A., Papavinasam, S., Michaelian, K., Omotoso, O., and Revie, R.W. "Effect of Field Operational Variables on Internal Pitting Corrosion of Oil and Gas Pipelines." <i>Corrosion</i> 65, 11 (2009): p.741. Papavinasam, S., Dorion, A., Li, J., Liu, P., and Park, D.Y. "Sour and Sweet Corrosion of Carbon Steel: General or Pitting, or Localized, or All of the Above?" CORROSION/2010, paper no. 10332. Houston, TX: NACE, 2010. S. Papavinasam, A. Doiron, and R.W. Revie, "Model to Predict Internal Pitting Corrosion of Oil and Gas Pipelines", <i>Corrosion</i> 66 (3), 2010, p. 35006 (11 pages). S. Papavinasam, A. Doiron, and T. Panneerselvam, "Integration of Localized Internal Pitting Corrosion and Flow Models", CORROSION 2012, Paper #23794, NACE International, Houston, TX (2012). S. Papavinasam, "Sour Localized Pitting Corrosion Model of Carbon Steel: A Status Update", CORROSION 2016, Paper no. 7250, Houston, TX: NACE (2016)	

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