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Development of a Model for Mitigated Corrosion – A Mathematical Model for Evaluation of Upstream Oil and Gas Field Applications that Include Mitigation by Corrosion Inhibition

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ABSTRACT

Over the past decades, several corrosion prediction models have been developed for Upstream Oil and Gas process conditions. These models provide the unmitigated corrosion rates in typical sweet or sour conditions. However, the practice of field operations is typically based on the mitigated corrosion rate. Therefore, the predicted unmitigated corrosion rates cannot directly be used to understand real-life situation unless the effect of mitigation is effectively considered. Currently, the mitigated corrosion rate is typically quantified via a very simplified method (e.g. corrosion inhibitor availability).

Corrosion prediction is designed to look forward and, ideally, should also be part of corrosion and asset integrity management. For this purpose, a robust analysis of the mitigation practices and methods is essential. This paper provides an overview of aspects to be considered when predicting mitigated corrosion rate for the case of continuous corrosion inhibitor (CI) injection as the mitigation barrier. It is proposed to use a combination of models to calculate the mitigated corrosion rate in a practical and reliable way. It is recognized that partitioning of the CI among different phases is a key aspect in relation to the field application of inhibitors. Therefore, guidance is provided to incorporate this as part of the corrosion mitigation and its prediction.

Key words: corrosion prediction, corrosion mitigation, corrosion inhibition, partitioning, modelling

INTRODUCTION

Corrosion Prediction

Due to the potential impact of corrosion in oil and gas production, the phenomena of CO₂ corrosion, H₂S corrosion and organic acid corrosion are heavily studied. For materials selection as well as asset

integrity and corrosion management, the threat of corrosion needs to be identified and evaluated, before mitigation strategies can be defined^[1,2]. For this purpose, a wide range of corrosion prediction models have been developed ^[3-30].

The following type of models can be distinguished:

- The earliest models, typically empirical and semi-empirical models for CO₂ corrosion^[3-7]
- Mechanistic models for corrosion tests-methods^[9] and later to real process flowing conditions^[10,11] and electrochemical models^[12].
- Inclusion of a wider range of relevant corrosion mechanisms^[8,14,19,20] first inclusion of organic acids^[8] and more recently H₂S corrosion^[15-17]
- Including specific phenomena like top of line corrosion^[24-30] and oil-wetting^[31,32].

There is still an ongoing effort to reveal and finetune the understanding of the mechanisms^[18,33-35] and improve their scientific background as well as their applicability.

Over the years, these corrosion prediction models have been used for several purposes:

1. For materials selection^[1,2], as a basis for the feasibility of the use of carbon steel.
2. For identification of requirements to design, corrosion allowance, pipe diameter, etc.
3. For identification of requirements to mitigation, corrosion inhibition (CI) injection design to meet availability requirements^[17,19-23], including method of injection (batch/continuous), frequency of treatment, cleaning, etc. For this purpose, models started using the mitigated corrosion rate as output.
4. For integrity evaluation, like direct pipeline integrity assessment (NACE SP 0110/0116), where also the mitigated corrosion rate has become the value to consider^[36,37,38].
5. Training corrosion engineers, where the use of models has been crucial in sharing knowledge and understanding the phenomena^[17,19].
6. And most recently there are requests to link the corrosion prediction models towards process control and integrity management.

Currently, corrosion prediction and its mitigation are often treated as two separate items, often even addressed by two different disciplines (e.g. prediction by materials and corrosion engineering and CI injection and selection by production chemistry). To be able to use corrosion prediction for asset integrity and corrosion management, the models should predict the corrosion at field conditions, which typically includes mitigation against the anticipated corrosion. The need for inclusion of corrosion mitigation, in particular the use of CI, is recognized with a limited focus previously. The models for corrosion mitigation are simply based on availability, batch inhibition, pigging treatment frequency, and linking to an unmitigated corrosion model^[17,19,20,21,23,39].

For microbial corrosion, a realistic corrosion prediction is not available. Instead, the focus has been on a prediction derived from the mitigation measures that influence a fixed corrosion rate^[19]. This non-scientific model is, nonetheless, practical in its use and provides clear operational guidance for engineers that work in projects and operations.

Recently a theoretical electrochemical model has been developed for CO₂ corrosion in the presence of a model CI^[40], this approach is mechanistic and is unique for different environments and chemicals. It is the first step and a follow-up could be of value for the development of a model for mitigated corrosion prediction, and CI selection and development.

What drives effective corrosion mitigation by corrosion inhibitors?

For the mitigation of CO₂/H₂S and organic acid corrosion by CI, there is no comprehensive and practical mitigated corrosion model available. The aim of this work is to develop such a model and identify the items that are vital to corrosion mitigation by CIs. This work links to the development of our internal corrosion prediction software package Hydrocor^{TM+}(HC), which includes a range of models for

corrosion prediction. In this paper, a review of what is already available and what requires additional effort for development is provided. In earlier work^[21,22,23,41], the wider scope of CI selection and corrosion management in upstream oil and gas production was addressed by introducing the definition of a CI-IOW (Corrosion Inhibition - Integrity Operating Window) as part of a robust CI selection and qualification. Derived from these papers, the following items are identified to be captured in a corrosion model that includes mitigation with CIs:

1. CI products have product-specific behavior that needs to be identified and captured as input to the model
 - a) Required CI concentration in the water phase $[CI]_w$, should be derived from the CI qualification program and results with a CI injection rate that ensures it.
 - b) Distribution of CI to the water phase and the substrate is vital for a successful corrosion mitigation program^[21,23,41-51]. Besides that, this behaviour is specific for each CI molecule (as part of the CI product), this is also a function of temperature, water chemistry (pH, salinity), and water cut / oil-water ratio.
 - c) Factors that play a significant role in the CI performance addressed in the CI-IOW should be included in the model, like T, P, pH, salinity etc..^[21,23,41]
 - d) Persistency can be very useful, and it would be beneficial to take it into account.
2. The unmitigated corrosion rate as defined by the current corrosion models can be used to identify the corrosion rates under non-effective mitigated conditions. However, be aware sometimes a failing CI can result in higher (in particular local) corrosion rates than, that without a CI, but this is not typical and can be addressed on a project-specific basis. In this work the models that are used include the following referenced models:
 - a) CO₂ corrosion model^[10,19]: this model will get an update with the latest insights on the mechanistic behavior^[18]
 - b) Organic acid model: the updated model includes the mechanistic model from CO₂ corrosion, but with a significant difference due to the particular behavior of organic acids and their buffer effect driving the corrosion rate. A range of models exist. The model use is not available in open literature.
 - c) H₂S corrosion model^[17]: this model already includes mitigation in particular for batch treatment and cleaning, which will not be altered and will, be included as is.
3. Flow can have a specific impact on CI performance, which requires attention including shear stress, water ratio, and dynamic water holdup and changes of process conditions along the process/pipeline. In this work the author used the flow model used is based a further development of the tool as included by Pots^[19]. Other effects that are included are top of line corrosion (and condensation) and water wetting^[32]
4. The availability concept^[19,20,39] is used for the uptime of effective CI injection (meeting the required dose rate as identified from items 1a and 1b above. Persistency in item 1d can be used with a link to the required injection availability.

Besides the CI-IOW items (as listed in 1c), other factors that can have an impact on CI performance are project-specific and not included in the model. These could be the presence of specific weld metallurgy, effectiveness under (sand) deposits, and compatibility with chemicals, which can and is typically addressed in a project-specific qualification program.

Similar to all corrosion predictions, the item even harder to get for corrosion mitigation is the quality of the data used as input, which remains crucial to the success of the corrosion prediction once deployed in practice.

A COMPREHENSIVE MITIGATED CORROSION PREDICTION MODEL FOR SYSTEMS USING CORROSION INHIBITORS

For the development of a model that predicts the mitigated corrosion rate that can be included in a software package, one can take the list from the previous section and identify an equation that addresses all the different input parameters. The process begins with drafting an overarching Equation (1) that includes all the different items that impact the mitigated corrosion and address the separate parts of the formula in subsequent steps.

$$CR_{mit} = fCR_{unmit} \cdot fFlow \cdot fChem \cdot fOil_{wetting} \cdot fCorr_{control} \quad \text{Equation 1}$$

The separate equations are listed in Table 1, providing the details on what could be used for each part of the equation. The HC software package includes a flow and chemistry model that links to the other models as part of the oil wetting and corrosion control factors, such as CI-IOW and water holdup. Fortunately, most of the equations can be addressed via existing models and items already available in literature and the HC software package. To keep the focus in this paper, we will address the available models by referencing them. The relation to corrosion control in this paper focuses on the effectiveness of mitigation by continuous CI injection, therefore:

$$fCorr_{control} = fCorr_{control, CI}$$

the details of this equation will be addressed later. When other control measures are selected or applicable in the project/asset, these should be defined and addressed with a different model.

Table 1: Background and required data required as input to Equation 1

Equation	Description	Available
$fCorr_{unmit}$	Unmitigated corrosion rate can be calculated via available corrosion prediction model (CO_2/H_2S /org. acid) including a Top of line corrosion model. In particular for sweet conditions, other publishes models are publicly available.	yes: [3,20] in HC
	Model required input: partial pressure of acidic gases pCO_2/pH_2S , water chemistry limits for chlorides/TDS including organic acids, alkalinity, temperature range, the link to the flow model provides a detailed corrosion rate profile.	
$fFlow$	A flow model is embedded in the tool for which an internal flow model for pipeline transport is used based on the identification of flow regimes, condensation rates, etc. However dynamic water holdup is not yet included and the development and prediction of it is rather complicated. However, for asset integrity and corrosion mitigation monitoring the value of the dynamic water hold-up could also come from in-situ process monitoring (as a plugin), this is available for some operating units. The availability of water hold-up data is crucial for the [CI]_w and prediction of the mitigated corrosion in particular for monitoring and a review of asset Integrity.	yes: in-HC issue dynamic Water hold-up
	Model required input: inlet temperature pressure, gas/oil/water flow, specific compositions, pipe design: diameter, pipeline profile, insulation (u-values) to determine condensation rates.	
$fchem$	A Chemistry model is needed to address the water chemistry and the changes in water chemistry including salinity, pH, etc. for this model an in HC available.	yes: in HC
	Model required input: the gas and water composition are crucial, especially total alkalinity and its balance with organic acids.	
$fOil_{wetting}$	A separate model for oil-wetting is in use ^[32] alternative models are available in literature as well ^[31] , if oil-wetting is present, the mitigated corrosion rate is 0. However, the operation conditions do not remain stable over field life typically.	yes: [32]
	Model required input: Flow of gas, water and oil, oil density, viscosity, and surface tension. Specific oil types might also include chemistries that might further stimulate oil-wetting, the current model might therefore in some cases be over-conservative, however, this data is also not typically easily available.	

For corrosion control using CI, the following items need to be included as listed in Equation 2:

1. What is the corrosion rate when the CI is effective (CI_{corr})?
2. What are the known limitations of the CI operating envelope? For which operation envelope was the CI qualified with a confirmed effective performance (CI-IOW)?

3. From the operation side, how effective is the CI dosed uptime of the injection system, typically expressed as availability? This can also be linked to the persistency of CI (CI_{operate})
4. Is the CI concentration in water ([CI]_w) on the required concentration? Have the dosage and process conditions been taken into account?

$$f\text{Corr}_{\text{control, CI}} = \text{CI}_{\text{corr}} \cdot f\text{CI-IOW} \cdot f\text{CI}_{\text{operate}} \cdot f[\text{CI}]_w \quad \text{Equation 2}$$

Table 2 list the items from Equation 2 and how they can be addressed.

Table 2: Background and required data as input to the Equation 2

Equation	Description	Available
1 CI _{corr}	Inhibited corrosion rate (at fully effective CI) derived from qualification testing and/or (reliable) monitoring should be typical 0.1 mmy ⁻¹ including localized corrosion (typically < 0.02 mmy ⁻¹ in electrochemical measurements) this section can also include the electrochemical model as defined by Domingues ^[40]	yes from testing
	Model required input: corrosion rate as determined from testing (should include evaluation of localized corrosion).	
2 CI-IOW	CI-IOW covers the operating envelope for which a CI product is qualified. A significant detail is provided in the earlier publication that outlines this concept ^[21,23] it is proposed to use this concept as input to the HC software interface to identify the limits for which the CI will be effective, operating outside those limits should set the mitigation to zero.	yes ^[21,23] from testing
	Model required input with acceptance criteria: partial pressure acidic gasses pCO ₂ /pH ₂ S, water chemistry limits for chlorides/TDS including organic acids, temperature range and wall shear stress.	
3 CI _{operate}	Availability of the CI injection and its persistency is data that covers the periods that the mitigation is effective, this will similarly be impacted during upsets, when [CI] _w is below target	
Injection availability %	Availability = 100% of uptime of the CI injection being on the target dose rate, details as outlined ^[19,20,39] In this model the input should be % of days per month having the CI injection working affectively with right dose rate, leading to the right [CI] _w .	yes ^[19,20,39] from operations
	Model required input: uptime data from the operator for targets of high availability remote and adjustable CI injection control might be required.	
Persistency	Persistency is the ability of the CI to continue its performance when [CI] _w is without proper dose rate ^[21,23,44] , this is typically a factor of days (typically max. 5 days for continuous CI injection). CI injection availability is typically reported on a monthly basis and can, for example, include benefits of persistency once per month (e.g. if qualification confirms 5 days complete persistency). The persistency can be used to increase a low availability with a maximum in the example of 16% (5/31), however one must be sure the total time per upset (over more months) does not exceed the CI persistency period	yes ^[21,23,44] from testing
	Model required input: Persistency should only be used if data can be provided that supports the performance of the CI in use, likely to be part of a CI qualification program ^[21,23] .	
4 [CI] _w CI concentration in water	The actual concentration of the CI in water ([CI]_w) should take into account the dose rate and the dynamic effects that influence the [CI] _w , especially changes in water cut. There is no established equation that can cover all applications, and this requires further detailed analysis to develop a model that can capture the effects of partitioning and flow. For this reason, the next section of the paper aims to address this remaining gap.	Not available, scope of paper
	Details will be given later in this paper, but from the literature, it can be seen that the concentration of CI in water depends on dose rate, CI distribution which seems to be chemical-specific and depend on process conditions ^[21,23,41-51] , water chemistry including pH and salinity/TDS (Total Dissolved Solids), temperature as well as the local water cut which is affected by water hold-up (condensing and dynamic)	Issues on CI distribution to be addressed

CORROSION INHIBITOR DISTRIBUTION

Background

In corrosion engineering, the [CI] (CI concentration) is often expressed in a partitioning coefficient (k_{part}) that would then be the ratio of [CI] in the water phase [CI]_w vs the liquid hydrocarbon phase [CI]_o,
[41,47,49,53]. see Equation 3

$$k_{\text{part}} = \frac{[\text{CI}]_w}{[\text{CI}]_o} \quad \text{Equation 3}$$

In other literature, the same concept is also mentioned as a partition coefficient (P) or distribution coefficient (D), which is the equilibrium distribution of a substance between two immiscible or partially miscible liquids.^[45] This concept assumes a constant value of concentration distribution based on equilibrium in the presence of two phases.

To understand [CI] distribution behavior, one must understand that interaction between phases will be disturbed by the bi-polar (surface active) nature of the CI molecules. In reality, particularly for surfactants, the distribution between water (polar) and oil (a-polar) is not likely a complete constant or provides ideal equilibrium behavior. The following items are identified that can influence the molecular distribution of CI between oil and water.

- A. Molecular partitioning is limited by micelle formation, at the CMC (critical micelle concentration), micelle formation starts that can shift the distribution towards the water phase.^[53] When emulsions are present, there may be the water/emulsion interface and emulsion/oil interface that could be required to include as well, see item B. In each case, the hydrophilic and hydrophobic portions of the molecule orientate accordingly, and at each interface, an equilibrium is established. Once the interfaces have been satisfied, any additional chemistry in the bulk fluids will form micelles.
- B. Adsorption at the oil/water interphase has been reported, where a plateau concentration can be reached in one of the phases and an Interphase can be formed with a high concentration of surfactants^[53] besides the interface mentioned at A. This can result in the formation of a separate phase as well.
- C. Chemical interactions/reactions (e.g. polar interactions, Lewis acid-base, and Ionic interactions), especially the ionic interactions are very relevant since a part of the CI molecule can be a salt (with a counter ion in water solution). The distribution of pure salts in the oil phase becomes neglectable compared to its solubility in water. This could also be a reason for a CI to accumulate at the interface, see item B. The frequently observed impact of water composition salinity and temperature might be also related to this item.
- D. Mixing and flow can shift the distribution and impact the presence of a phase beyond its normal preference (even oil in water). For example, it can result in a mixture of phases rather than 2 separate phases and droplet distribution between the phases (e.g. [CI]_o droplets or microemulsions dispersed in the aqueous phase, mixing of the oil/water interphase onto the substrate) Also with sufficient mixing in some cases more oil-soluble CI products can be used, however in those cases the effectiveness on CI performance becomes very much flow dependent, which might not be easily assured over the field life.
- E. CI products are a mixture of species that individually can show differences in distribution behavior (including influencing each other). Also, some molecules might provide different interactions than others.

Besides the above examples, a wide range of conditions can impact the distribution of CI molecules, where intermolecular interaction (e.g. van der Waals, polar interactions, Lewis acid-base, hydrogen bonds) as well as macro interaction (e.g. mixing, flow, shear, temperature) can dominate the actual distribution under process conditions.

In relation to the effect of ionic solutions and micelle formation, a wide range of adjustments to Equation 3 has been developed^[53], including the incorporation of activity coefficients and micelle behavior. However, for practical oil and gas operations, the prediction models seem to be complicated. The required data is rarely available. Since CI products typically hold a confidential composition, and operational conditions and compositions might not be available in detail and a simplified model (with straight forward input parameters) would be preferred. More efforts to further gain detailed understanding would add significant value in understanding the nature of CI distribution.

From day to day experience as well as from literature for CI testing and deployment, it can be concluded that the equilibrium concept (following Equation 3) seems in reality also not easily applicable. Besides the fact that process conditions are far from constant, [CI]_w has shown to be