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Corrosion Prediction for Corrosion Rate of Carbon Steel in Oil and Gas Environment: A Review

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A B S T R A C T

Corrosion predictions are essential for corrosion and material engineers. It is used to prepare pre-Front End Engineering Design (pre-FEED). FEED guides to select appropriate materials, planning test schedule, work over management, and estimate future repair for cost analyses. Corrosion predictions also calculate life of pipeline and equipment systems during operational stages. As oil and gas environments are corrosive for carbon steel, it is important to account the corrosion rate of carbon steels in those environmental conditions. There are many existing corrosion predictions software, which are available in oil and gas industries. However, corrosion predictions only can be used for particular ranges of environmental conditions because they use different input parameters. To select the most applicable of corrosion predictions software, engineers have to understand theoretical background and fundamental concept of the software. This paper reviews the applications of existing corrosion prediction software in calculating corrosion rate of carbon steel in oil and gas environmental systems. The concept philosophy of software is discussed. Parameters used and range of conditions are also studied. From the results of studies, there are limitations and beneficial impacts in using corrosion software. Engineers should understand the fundamental theories of the corrosion mechanism. Knowing limitations of the models, the appropriate model can be correctly selected and interpretation of corrosion rate will close to the real data conditions.
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A R T I C L E   I N F O

1. INTRODUCTION

Corrosion rate in oil and gas industries involve complex factors (Kurniawan, *et al.,* 2016). Those models basically are focused on CO_2 environments (Asmara & Ismail, 2011a).

The additional factors such as H_2S, H_2S scaling effects, oil wetting effects, multiphase flow, precipitation of corrosion product films, inhibitor are, sometimes, also accounted in predictions (Asmara, *et al.,* 2011b).

Because concepts and methods to predict corrosion rate are calculated in different ways, it is frequently found that there are differences of the corrosion data calculated by different models under nearly identical conditions. Some models provide over-estimate of corrosion rates than others(Leong, *et al.,* 2016). Corrosion models are formulated using various scenarios among theories and experiments (Alia, *et al.,* 2017). Those models use parameters and formulas from literatures, experimental data and their own experiences to calculate corrosion rate data (Asmara, *et al.,* 2013). The types of corrosion models can be classified into three types. The first is mechanistic models which uses theoretical background and physical formulas to express the mechanisms of corrosion reactions. Secondly is empirical corrosion prediction model (Asmara, & Ismail, 2012). It is developed based on best-fit parameter in experimental regression. And the third is semi empirical models (Asmara, *et al.,* 2016). This model is developed using parameters and formula from literatures and based on the researchers' experiences. The models are also useful to manage corrosion protection strategy for the life of the metallic structural by optimizing the correct material selections. Thus, it is essential to use the appropriate corrosion model which is suitable for certain conditions in order to obtain correct corrosion rate data. So, the most cost-effective is achieved.

2. MECHANISTIC MODELS

The main concepts of mechanistic models are using electrochemical reactions and physical changes of mechanism formulas (Asmara & Ismail, 2007). They includes state properties, thermodynamics theories of all species. It includes electrochemical reactions and diffusion process. Mechanistic model states that corrosion process covers mass transfer (diffusion), electrochemical reactions which are oxidation/reduction reactions. The model focuses on cathodic and anodic reactions which occur in the system involving several species. The mechanism of anodic dissolution depends on the dissolution rate and on the activity of hydroxide ions. While cathodic processes are related to the reduction of the species involved. Examples of mechanistic corrosion models are models derived by (de Waard & Milliams, 1975; Nesic 2007), etc.

2.1. Electrochemistry Processes

To investigate the corrosion mechanisms, electrochemical processes consider metal surface reactions which are transport process for each species that involves in the reactions. The model focuses in cathodic and anodic reactions which happen in the systems. The electrochemical is chemical reactions where electrons are transferred between molecules which is called oxidation/reduction reactions in anodic and cathodic site (Nordsveen, *et al.,* 2003).

2.2. Anodic Reactions

In anodic reactions, there is dissolution of metal. It is around the corrosion potential which can be under activation control or passivation process. The mechanism of activation control was proposed by (Bockris, *et al.,* 1961). Anodic charge transfer in carbon steel is expressed as (Wang, 2002):

$$i_{(Fe)} = i_{Fe}^o \exp\left[\frac{-\alpha_{Fe}F\left(E - E_{Fe}^o\right)}{RT}\right] \quad (1)$$

$$i_{Fe}^o = i_{Fe}^* a_{OH} a_{H_2O}^{1.6} \quad (2)$$

2.3. Cathodic Reactions

In metallic corrosion, cathodic processes are due to the reduction of separate species, i.e., H^+, H_2O, H_2CO_3 and HCO_3^-. In acidic solutions, the reduction of H^+ is the dominant cathodic reaction. There are two possibilities

reactions in cathodic site, which are diffusion limiting current density and activation current density. Activations current density are given by expression (Wang, 2002):

$$i_{H,a} = i_H^o \exp\left[\frac{-\alpha_H F\left(E - E_H^o\right)}{RT}\right] \tag{3}$$

The exchange current density is given by

$$i_H^o = i_H^* a_H^{0.5} a_{H2O}^{2.2} \tag{4}$$

where a_H is activation of hydrogen ions and a_{H2O} is activation of H_2O.

The limiting current density results from diffusion-limited transport of protons to the metal surface and can be calculated as

$$i_{H,\lim} = K_m F a_H \tag{5}$$

where km is the mass transfer coefficient. The value of km can be calculated if the flow regime, diffusion coefficient of H^+ ions and solution viscosity are known.

2.4. Scale formation

In the case of corrosion product on the metal surface with film formation, it can be expressed mathematically. These corrosion mechanisms are based on several assumptions which can be described as follows: convective diffusion, molecular diffusion, and diffusion via solid film. Corrosion mechanism which happens in solutions as a combination of mix gases can be expressed from the following equation. This expression is the case of corrosion rate of steel due to mixed species (Wang, 2002).

$$CR_i = A_i e^{\frac{B}{RT_K}} \ln \frac{c_{b,i} - CR_i\left(\frac{\delta_{oc}}{D_i \varepsilon \Psi} + \frac{1}{k_{m,i}}\right)}{c_{s,i}} \tag{6}$$

where K_m is the mass transfer coefficient of species i (m/s). C_b is the bulk concentration of species i (mol/m^3), C_o is the interfacial concentration of species i at outer scale/solution interface (mol/m^3), D_i is the diffusion coefficient for dissolved species i (m^2/s), ε is the outer scale porosity, ψ is tortuosity factor, C_i is interfacial concentration of species i, δ_{os} is the thickness of outer film scale, δ_{hbl} is the turbulence boundary layer thickness, δ_{mbl} is the mass transfer boundary layer thickness, δf is the film thickness, A is the Arhrhenius constants, T_k is the temperature (Kelvin), and c_s is the surface concentration.

3. CORROSION PREDICTIONS SOFTWARE

Many industrial corrosion companies produce corrosion predictions software, which are based on empirical models and combination of empirical and mechanistic approach. Empirical corrosion prediction models are developed based on best-fit parameter in experimental regression so called Semi-empirical models. The semi empirical models are developed using parameters and formula from literatures combined with their experimental data. In oil and gas industries, there are many corrosion productions software. These include Norsok, Cassandra, Electrochemical Corrosion Engineering (ECE), Ohio Model etc. They develop models by using their own experiments, field data combined with fundamental formulas and its many subsequent derivatives. All of these were developed based on different systems and assumptions.

3.1. NORSOK

The NORSOK standard is owned by Norwegian Oil Industry Association and Federation of Norwegian Manufacturing Industries. The program covers only calculation of corrosion rates where CO_2 is the corrosive agent. It does not include the corrosivity, e.g. contamination of O_2, H_2S etc. The model is an empirical model for CO_2 at different temperatures, pH, CO_2 fugacities, wall shear stresses, and temperatures from 20 to160°C. The model calculates pH and wall shear stress. The effect of acetic acid is not account for in this model, but it is still valid to predict corrosion rate if the concentration of acetic acid is less than 100 ppm.

3.2. ECE (Electronic Chemical Engineering)

ECE program software calculates corrosion rate based on the modified model by (de Waard & Milliams 1975). ECE model includes oil wetting correlation based on field correlation. ECE proposes a corrosion prediction expression using corrosion reactions and mass transfer effects. The mass transfer represents the main part of the dependence on flow velocity and pipe diameter. In ECE, they develop corrosion prediction by involving several variables such as gas fugacity, formation of protective films, effect of ferrous ions, presence of oil, effect of condensing water, and effect of multiple phase.

3.3. Cassandra (DWM 93)

Cassandra is a model developed based on the experiences of (de Waard & Milliams 1975). The input includes pH, CO_2 concentration, temperature, and water contaminant. This model does not consider scaling temperature. The user must set an assumption of the scaling temperature. This model has important aspects which influence rate of corrosion, namely corrosion inhibitor availability and corrosion risk categories. The model also accounts for the presence of acetate in water as acetic acid. The major input to the model are: CO_2 mole %, temperature, total pressure, liquid velocity and water chemistry. Besides that, the model has secondary input, such as hydraulic diameter and glycol concentration, oil type (crude or condensate) and water type (condensed water or formation water). The effect of oil wetting in this model is not included.

3.4. Parameters Comparison of NORSOK and CASSANDRA Models

Both NORSOK and Cassandra have limitations in predict the corrosion rate. **Table 1** shows the parameter comparison between NORSOK and Cassandra models.

3.5. Experimental Corrosion Predictions Models in Oil and Gas Environments

The corrosion mechanism of mild steel in the presence of CO_2 in various conditions has been a widely reviewed by researchers. Tthere are many experiments and field studies have been conducted. The initial studies in CO_2 corrosion was conducted by (de Waard & Milliams 1975) that have become a fundamental concept for the further studies on the CO_2 corrosion phenomenon. The newest of corrosion mechanism was studied by (Nesic & coworkers 2007) who have claimed to be successful in modeling CO_2 corrosion rate based on theoretically. **Table 2** compiles corrosion predictions formulas based on experimental data.

3.6. Effect of Flow in Corrosion Modelling

Effect of flow on steel corrosion is a type of corrosion caused by a combination between mechanical and electrochemical effects (Silverman, 1988). Mechanical effects due to water motion causes impingement that leads to metal removal and material

abrasion. Water that flows to the surface can wear the corrosion product film or create shear stress to the surface. Thus, corrosion will occur faster (Eisenberg *et al.,* 1954). Corrosion rate also can increase due to effects of differences in velocity turbulence across the surface. Parameters that influence flow induced corrosion are hydrodynamic boundary layer and rate of momentum transfer from the bulk to the wall. In this conditiion, corrosion may be controlled by the rate of mass transfer of a reactant or the rate of corrosion products. As calculated by two models, they are confirmed that increasing flow rate corrosion rate will also increase. However, empirical model calculates corrosion rate higher than freecorp model. Empirical model states that increasing flow, corrosion rate continues increase, while freecorp finds that the highest corrosion rate occurs at 1000 rotation speed. FreeCorp indicates that when rotation speeds are more than 1000 rpm, corrosion rate will remain constant which refers to limiting current density (Silverman, 2004).

Table 1. Comparison Parameters considered in some corrosion predictions software (NORSOK, ECE, FreeCorp, and Cas-sandra)

Parameters	Corrosion prediction software			
	ECE	Norsok	Cassandra	FreeCorp
Temperature (C)	√	√	√	√
Total Pressure (bar)	√	√	√	√
Total mass flow	√	√	N/A	√
CO_2 fugacity (bar)	√	√	N/A	√
Wall Shear Stress (pa)	√	√	N/A	√
pH	√	√	N/A	√
Glycol concentration	√	√	N/A	√
Inhibitor efficiency (%)	√	√	N/A	√
Diameter (mm)	√	√	N/A	√
Liquid velocity (m/s)	√	√	√	√
H_2S	√	N/A	N/A	√
Pipeline orientation	√	N/A	N/A	N/A
Polarization graph	N/A	N/A	N/A	√
Formation water/condensed water	√	N/A	N/A	N/A
Types of materials	√	N/A	N/A	N/A
Cost analyses	√	N/A	N/A	N/A
Length of pipelines	√	N/A	N/A	N/A
Oil contents	N/A	N/A	N/A	√

Table 2. Corrosion formulas calculated using some experimental data

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$CR = e^{-9225/T} x10^{-pH} x5.848x10^{17}$
For worst case calculation of the corrosion rate (CR) of low alloy steel in slightly sour conditions

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$$CR = 31.15\, Cr_{freq}Cr_{crude} \left(\frac{\Delta P}{L}\right) 1^{0.3}W^{0.6}P_{CO2}^{0.8}Te^{-2671/T}$$
Crude oil type and water cut (W<30%)
$$CR = 31.15\, Cr_{freq}Cr_{crude} \left(\frac{\Delta P}{L}\right) 1^{0.3}W^{1.6}P_{CO2}^{0.8}Te^{-2671/T}$$
Crude oil type and water cut (W>30%)
CR is corrosion rate (mm/yr), *ΔP/L* is the pressure gradient (N/m³), *W* is water cut, *PCO₂* is partial pressure of carbon dioxide (MPa), *T* is temperature (K), *Cr_crude* is factor to account for crude oil type, based on (0< *Cr_crude* <1), *Cr_freq* (= 0.023 (F) + 0.35) is the normalized factor to account for slug frequency (0< *Crfreq* <1), and *F* is slug frequency to a maximum of 35 slugs/minute.

V_cor = 31.15 Cr_freq Cr_oil (0.38 Fr)0.3 wc^0.6 PCO₂^0.8 T exp(-2671/T)
where *Crfreq* is term for slug frequency, *Croil* is term for crude oil type, *wc* is water fraction (%), *T* is temperature in K, *Fr* is Froude number in the liquid film defined as: *Fr is (Vt – Vf) / (g hf)0.5 (10)* with *Vt* is translational velocity of the slug (m/s), *Vf* is average velocity of the stratified liquid film (m/s), *G* is acceleration due to gravity(m²/s), and *hf* is effective height of the liquid film.

CR = 8.6988 +9.856x10⁻³ (O₂)-1.48x10⁻⁷(O₂)- 1.30865(pH) +4.934x10⁻²(CO₂)(H₂S)-4.8231x10⁻⁵(CO₂)(O₂)-2.372x10⁻³(H₂S)(O₂)-1.113x10⁻³(O₂)(pH)
where *CR is general corrosion rate, (O₂) is O₂ concentration of gas (ppmv), (CO₂) is CO₂ concentration of gas (psi), H₂S is H₂S concentration of gas (psi), pH = pH initial*


$$CR = 31FF \left(\frac{\Delta P}{L}\right) 1^{3.3}W^{1.6}P_{CO2}^{0.8}Texp^{-2671/T}$$
CR is general corrosion rate, *FF* is the frequency factor, *(DP/L)^0.33* is the flow pressure gradient in Pascal/meter, *(PCO₂)^0.8* is the CO₂ partial pressure in MPascal, *T* is the Kelvin temperature.

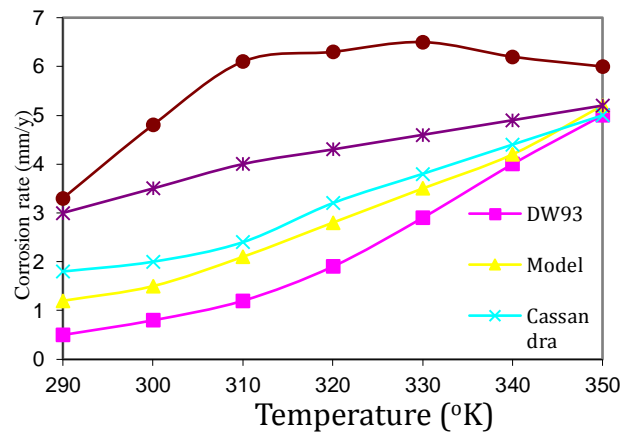## 3.7. Effects of Temperature on Corrosion Rate of Carbon Steel

In oil and gas environments (CO_2 system), temperature affects the conditions for formation of the protective carbonate layers and affects corrosion rate in a different manner. At temperatures lower than 60 °C, the solubility of $FeCO_3$ is high and the precipitation rate is slow; thus protective films will not form until the pH is increased more than solubility product (Nafday, 2004). Above 60°C the solubility of $FeCO_3$ decreases and the protectiveness of the iron carbonate layer increases with temperature; thus, the corrosion rate is reduced. Scaling temperature is the temperature where corrosion rate reaches a maximum value.
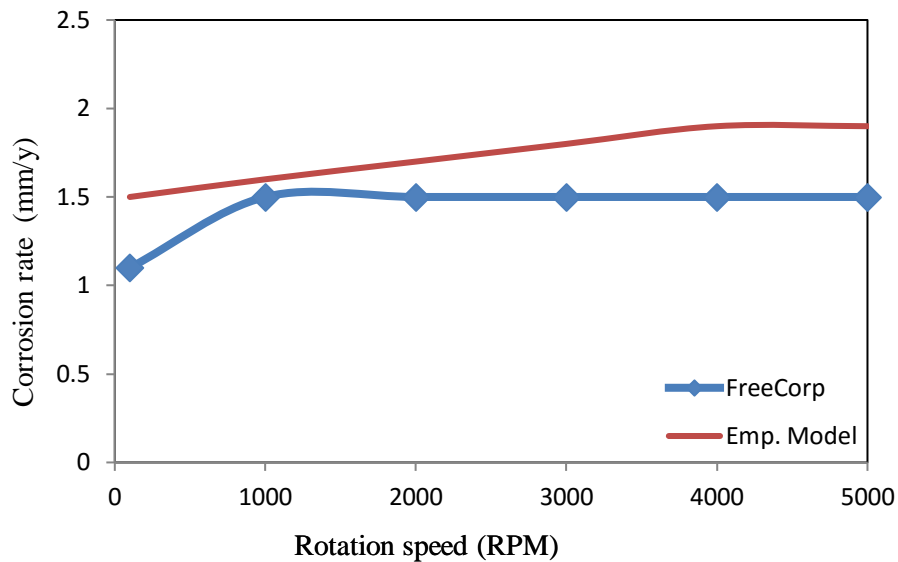
Figure 1. Effects of flow on corrosion rate as calculated by empirical model and FreeCorp model.

Figure 2 shows corrosion rate of carbon steel in CO2 environments at 1 bar and pH 5. Models of corrosion prediction provide different values. The most conservative is obtained by Cassandra model. And the lowest corrosion rate is calculated using norsok software. From the figure, it is clearly that all of software shows increasing of corrosion rate when temperature increases. Only Cassandra states that corrosion rate increases until temperature 60°C. It tends to decrease when temperature exceeds 60°C. The temperature is called as scaling temperature. From the figure, it also shows that there are obvious differences among the models. It means that understanding effects of temperature on corrosion rate are still under debatable. Every models uses different approach to count corrosion rate. The differences come from different assumption regarding effects of film formation, quality of film, solubility of $FeCO_3$, saturation of pH, water cut, interaction among species (Silverman, 2004).

Figure 2 Comparison effects of temperature on corrosion rate of carbon steel at pH5 and 1 bar as calculated by some corrosion models.

4. EFFECTS OF pH

pH is an important parameter for corrosion process. Normally, corrosion rate will be lower at higher pH,. The pH of a wet gas in CO_2 system is often assumed as equal to the saturation of $FeCO_3$ precipitation. **Figure 3** shows the predicted corrosion rates as effects of pH which differs depending on the models.
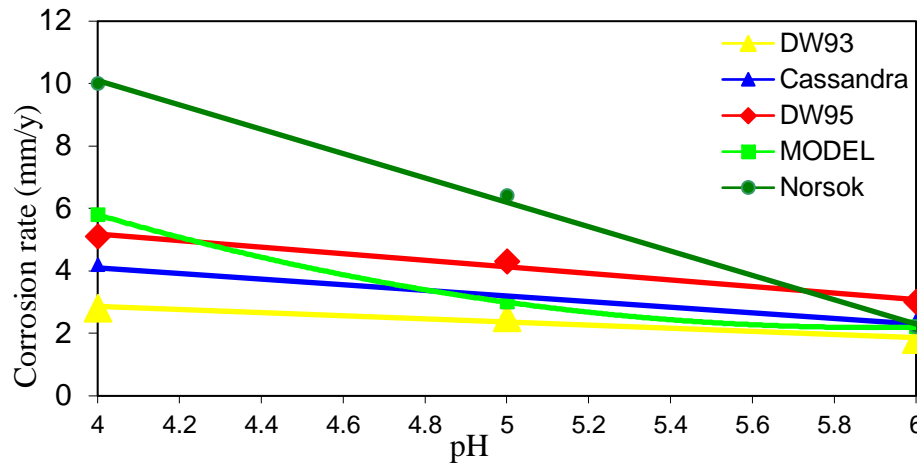
Figure 3 Comparison effects of pH on corrosion rate of carbon steel at pH5 and 1 bar as calculated by some corrosion models.

From the figure, corrosion predictions software present large difference when pH is 4. But at pH 6, almost all models give the same values. These are because various assumptions in calculating corrosion rate as effects of pH. The pH in CO_2 system is often assumed as equal to the saturation of $FeCO_3$ precipitation. The pH can also be calculated by involving the concentration of species such as CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}, H_2S, HS^-, S^{2-}, H^+, OH^-, H_2O, Fe^{2+}, CH_3COOH (acetic acid), CH3COO⁻. Sometimes, pH calculation can be done by incorporating the $FeCO_3$ precipitation kinetics. The pH is also influenced by H^+ ions concentration, temperature, pressure, and ionic strength. Thus pH in calculation can be different among the models software. Dissolved iron bicarbonate as the initial corrosion product will also contribute to increase the pH of solution.

Design of Experiment (DOE) and Statistical Modeling for CO_2 System

Recently, empirical models of corrosion processes have been used to predict corrosion process involving several independent variables. However, most of the empirical models do not predict the corrosion rate in several variables simultaneously (Mokhtar, 2005). Using empirical methods, modeling interactions effects among the species and the operational conditions simultaneously, require large number of experiment which is costly and takes time. These limitations can be overcome by using design experiment of response surface methodology (RSM). This is a simple method and believed can represent overall unselected variables.
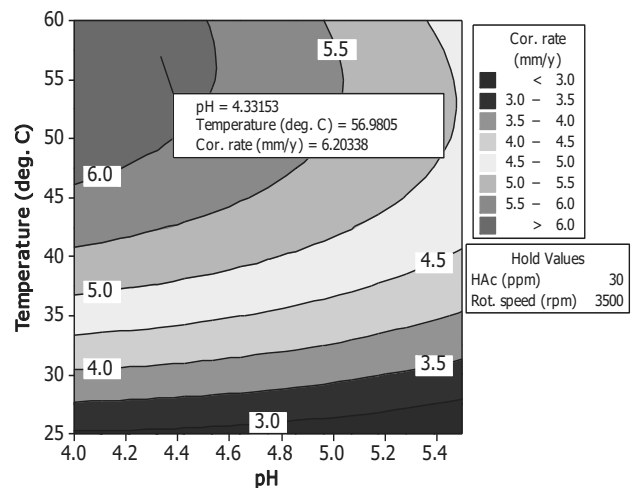

Figure 4. Response surface graph for corrosion rate as a function of temperature and pH (HAc at 30 ppm and rotation speed at 3500 rpm).

The application of RSM allows visualization of the experimental results in a 3-D

display. RSM is used to determine optimal levels for variables input. RSM is a sequential procedure for constructing empirical relation for the experimental data. Using response information, the optimum data between factors can be developed and model improvements can be achieved. It has been proven that researchers have used response surface method (RSM) to process data systematically that can allow to apply multiple regression simultaneously. Response surface design methodology is also often used to refine models to obtain an optimum design. RSM is useful to obtain critical points in the experimental variables. The surfaces generated by linear or polynomial models can be used to indicate the direction in which the original design must be started to attain the optimal conditions. For polynomial models, the critical point can be characterized as maximum, minimum, or saddle. Using RSM, it is possible to calculate the coordinates of the critical point through the first derivative of the mathematical function (Asmara, *et al.,* 2017). First derivative equals to zero indicates that critical points is located. They have studied corrosion rate in CO_2 environments by using RSM successfully (Mune, *et al.,* 2008). They are all claim that RSM can reduce number of experiments with satisfied results.

5. CONCLUSION

There are differences of corrosion rate predicted by various corrosion models. Variations of results are caused by assumptions made by corrosion models. Particular parameters such as H_2S concentration, scale effects, effects of wall shear stress and hydrodynamic condition of the solutions conditions will impact on results. ECE and FreeCorp are the models with more parameters inputs. These two models are flexible which can be applied for any environmental conditions. Other model like Cassandra gives more conservative which contribute a greater over design. Empirical methods combined with RSM propose improvements techniques. RSM can overcome limitation of pure empirical methods by simplifying experiments models. Selecting the best corrosion models require further interpretation to explain real conditions, thus mechanistic methods are more realistic. The user should also understand comparison regarding limitation, advantages and scope of assumptions of the models to obtain appropriate data.

6. ACKNOWLEDGMENTS

7. AUTHORS' NOTE

The author(s) declare(s) that there is no conflict of interest regarding the publication of this article. Authors confirmed that the data and the paper are free of plagiarism.

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