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Mathematical modeling of CO_2 corrosion with NORSOK M 506

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Abstract

The consequences of corrosion are catastrophic. Also costs to the global economy reached "$2.5 trillion, or world GDP's 3.4%". Despite the magnitude of the corrosion cost, it can be concluded that scientific studies on corrosion prevention are quite limited, except for high-risk sectors such as aviation and the fuel oil industry. It is important to fight against corrosion to ensure the safe operation of oil-carrying pipelines under the sea, and to prevent accidents and environmental damage. As a result of developing industry conditions and increasing needs, modeling corrosion is a very effective method for the prevention of corrosion. Industry, research companies, and universities have developed many corrosion rates and prediction models. One of them is the NORSOK M 506 model. In this study, the NORSOK M 506 CO_2 corrosion prediction model and the experimental results conducted by Nešić, Solvi and Enerhaug in 1995 were compared in terms of CO_2 corrosion rate. The results showed that the mathematical corrosion model calculated nearly six times higher than the experimental studies.

1. Introduction

The use of large-diameter, thin-walled pipes in pipeline transportation to meet the rapidly growing demand for oil and gas resources has also increased the risk of high pressure operations. However, undersea oil transportation poses a serious threat of corrosion due to the difficult operating conditions. The Pipeline and Hazardous Materials Safety Administration (PHMSA) of the United States Department of Transportation (USDOT) stated 18% of major accidents in the United States of America (USA) between 1988 and 2008 were due to corrosion of the equipment [1]. Accidents such as Flixborough, (the UK, 1974), Berre l'Etang (France, 1988), Kallo (Belgium, 2005) and Gironde (France, 2007) highlight the potential for serious consequences of serious accidents [2]. Aside from the fact that approximately 40% of the pipelines around the world have reached the end of their design life, when corrosion in the pipelines considered, it would be fair to say that it is possible to have a major accident in the oil industry at any time. The number of incidents may increase in pipelines that have reached the end of their design life, as internal corrosion poses an increasing threat over time [3]. The corrosion cost worldwide is $2.5 trillion, which corresponds to 3.4% of the world's GDP [4]. Considering that Italy ranks eighth among the ten most developed countries in the world with a gross product of $2.5 trillion, the importance of cost reduction can be better understood [5]. The National Society of Corrosion Engineers (NACE) published a research report titled International Measures of Prevention, Application, and Economics of Corrosion Technologies (IMPACT). The report concluded that studies on corrosion prevention will reduce the cost by between 15% and 35% [4]. This is a valuable ratio when dealing with an inevitable phenomenon like corrosion.

When fighting against corrosion there are several methods such as safety in design in the

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industry, choosing the right material, strengthening the material, changing the ambient conditions (inhibitor addition, reducing the temperature and speed), cathodic and anodic protection, coating, modeling of corrosion damage, development of environmentally friendly economical corrosion protective materials like chromium despite its toxic, carcinogenic health effect [6] and coatings. Modeling operation conditions and accelerated corrosion tests in the laboratory environment may help to predict estimation of the remaining time to the major repair or replacement of equipment/material.

As a result of developing industry conditions and increasing needs, modeling prevention of corrosion. Despite the magnitude of corrosion is a very effective method for the corrosion cost, it can be concluded that scientific studies on corrosion prevention are quite limited, except for high-risk sectors such as aviation and the fuel oil industry. *European Union (EU) Major Accident Reporting System (eMARS)* database stated that 20 percent of the 137 major refinery incidents, that occurred since 1984 have been caused by corrosion [7]. When the accidents caused by corrosion in the oil industry are considered, as seen in Figure 1, pipelines take the first place in the equipment list covering the most frequent accidents [8].

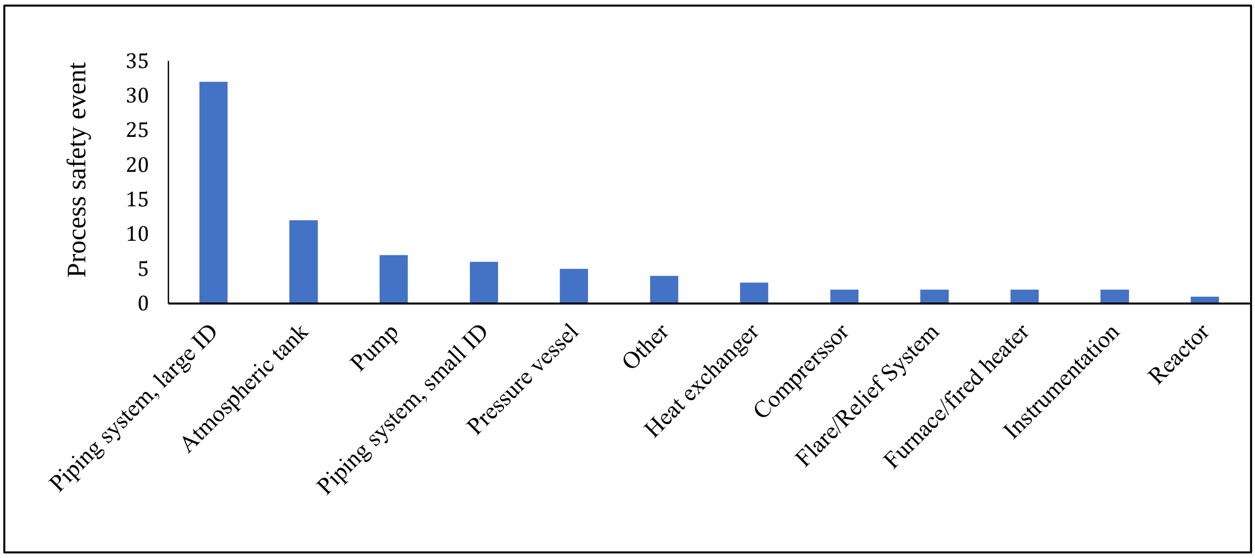

Figure 1. The number of process safety events (Tier 1) by equipment, redrawn from reference, redrawn.

Corrosion occurs both inside and outside of oil subsea pipelines, although the most intense corrosion occurs outside of the pipe, internal corrosion has gained importance since it is related to the design life. Internal corrosion involves high risk due to the nature of the transported materials, the presence of water, and dissolved gases such as CO_2 and H_2S. Crude oil is not corrosive, but they cause corrosion when electrolytes such as water are present in the environment [9]. The most common types of corrosion are organic acid, H2S, The use of large-diameter, thin-walled pipes in pipeline transportation to meet the rapidly growing demand for oil and gas resources has also increased the risk of high pressure operations. However, undersea oil transportation poses a serious threat of corrosion due to the difficult operating conditions. The Pipeline and Hazardous Materials Safety Administration (PHMSA) of the United States Department of Transportation (USDOT) stated 18% of major accidents in the United States of America (USA) between 1988 and 2008 were due to corrosion of the equipment [1]. Accidents such as Flixborough, (the UK, 1974), Berre l'Etang (France, 1988), Kallo (Belgium, 2005) and Gironde (France, 2007) highlight the potential for serious consequences of serious accidents [2].

Aside from the fact that approximately 40% of the pipelines around the world have reached the end of their design life, when corrosion in the pipelines considered, it would be fair to say that it is possible to have a major accident in the oil industry at any time. The O_2-induced corrosion, and sweet corrosion (CO_2 corrosion) [10], [11]. As a result of developing industry conditions and increasing needs, modeling of corrosion damage emerges as a very effective method in the prevention of corrosion. To obtain a more accurate estimation rate for CO_2 [11]. Despite all these developments, corrosion rate prediction still exists as a problem to be solved for industries with high operational risk.

Although many papers studied NORSOK M506, the exact difference between experiment and mathematical modeling is still unknown. In this study, corrosion rate calculation was performed with the NORSOK M 506 model developed for modeling CO_2 corrosion and compared with the data collected with Nešić, Solvi and Enerhaug's (1995) experimental study [12]. With this approach, it is aimed to determine the difference between the experimental and mathematical corrosion rate estimation for high operational risk processes.

2. Material and Method

2.1. Nešić, Solvi and Enerhaug's experiment

In this study, the data from the experimental study [12] conducted by Nešić, Solvi and Enerhaug in 1995 were used. The corrosion rate was monitored using corrosion polarization resistance (LPR), potentio-dynamic scavenging and electrochemical impedance techniques. The research was intended to see how flow affected carbon dioxide corrosion in the lack of protective surface films. It has been trying to come up with solutions to the problems associated with the transportation of the oil and gas industry. Nešić et al., 1995 studied temperature, pH, and velocity effect on corrosion, a wide range of parameters ranging from laminar flow to highly turbulent flow were studied in test sections consisting of rotating cylinders and pipes: Temperature T=20-80°C, pH=4.0-6.0, partial pressure of CO_2 P_{CO_2} =1 bar (100 kPa) and partial pressure of H_2S P_{H_2S}=0 bar, velocity v=0-13 m/s, [NaCl]=1%, [HAc]=0 ppm, [Fe^{+2}]<1 ppm. The experiments are repeated several times, replicated and derived from LPR measurements confirmed by weight loss measurements. The test dataset used in theoretical calculation from the experiment was shown in Table 1 [12].

Table 1. Test dataset used in theoretical calculation from Nešić et al. 1995.

Parameter	Value
Test solution	Ionized water, CO_2 gas weighted 1% NaCl
Temperature (°C)	20, 50, 80
pH	4, 5, 6
CO_2 partial pressure (bar)	1
Flow rate (m/s)	2-12

2.2 NORSOK CO_2 corrosion model

The Norwegian petroleum industry created the standard NORSOK M 506 model to calculate the corrosion rate caused by CO_2 in hydrocarbon production and processing systems. The CO_2 corrosion rate at a place with temperature T is calculated using the NORSOK M 506 model. To make an ideal and safe design in multi-phase turbulent flow in subsea oil pipelines, the effects of operating parameters on pressure gradient, water cut and flow model should be investigated. In most experimental approaches, studies that can fully address these issues are limited. The model was created from the data obtained during the calibrating of the De Waard model [12], [13]. It allows the corrosion rate to be determined at temperatures between 5-150°C. The model revealed that the corrosion rate along the pipeline always decreases.

The model results were validated and verified by the experimental data. The model is made up of three empirical equations that calculate the corrosion rate in mm/year depending on the temperature range. Equation (1) is as the following [14].

$$CR_T = K_T \times f_{CO_2}^{0.62} \times \left(\frac{\tau}{19}\right)^{0.146+0.0324\ log(f_{CO_2})} \text{x} f(pH)_T \qquad (1)$$

CR_T, rate of corrosion in mm/year; K_T, the equilibrium constant at temperature T; f_{CO_2}, fugacity in bar; τ, shear stress Pa, pH-dependent function $f(pH)_T$ at temperature. K_T is a linear variable and changes depending on the temperature, presented in Table 2, T is the temperature in Celsius [14].

Table 2. Variation of K_T with temperature.

T (°C)	K_T	T (°C)	K_T
5	0.42	80	9.949
15	1.59	90	6.250
20	4.762	120	7.770
40	8.927	150	5.203
60	10.695		

The fugacity of CO_2 decreases with increasing temperature. Since pressure drops throughout the pipeline and due to high dependence on the system pressure (P), the fugacity diminishes with distance while the partial pressure (P_{CO2}) is assumed to be constant. The fugacity f_{CO2} in the NORSOK model, is calculated by following equations (2) and (3) [14].

$$f_{CO_2} = a \times P_{CO_2} \quad (2)$$

$$P_{CO_2} = CO_2\% \times P \quad (3)$$

In equations (2) and (3), f_{CO_2} is CO_2 fugacity, a fugacity constant, and P_{CO2} CO_2 partial pressure In equation (4) and (5) T_k is the temperature in Kelvin. The fugacity constant varies according to the pressure value [14]:

$$a = 10^{P(0.0031-1.4/T_k)} \text{ P} \leq 250 \text{ bar (25 000 000 Pa)} \quad (4)$$

$$a = 10^{250(0.0031-1.4/T_k)} \text{ P} > 250 \text{ bar (25 000 000 Pa)} \quad (5)$$

pH is critical for corrosion calculation. In NORSOK M 506 corrosion model, variables in Table 3 are used to calculate pH effect ($f(pH)_T$) between temperature of 5-80°C [14]. For higher temperatures (90, 120, and 150°C) pH function is divided into three different pH ranges as shown in Table 4 [14].

Table 3. Equations for pH effect $f(pH)_T$ calculation.

T \ pH	$3.5 \leq pH < 4.6$	$4.6 \leq pH < 6.5$
5	$f(pH) = 2.0676 - (0.2309 \times pH)$	$f(pH) = 4.342 - (1.051 \times pH)(0.0708 \times pH^2)$
15	$f(pH) = 2.0676 - (0.2309 \times pH)$	$f(pH) = 4.986 - (1.191 \times pH) + 0.0708 \times pH^2)$
20	$f(pH) = 2.0676 - (0.2309 \times pH)$	$f(pH) = 5.1885 - (1.2353 \times pH) + (0.0708 \times pH^2)$
40	$f(pH) = 2.0676 - (0.2309 \times pH)$	$f(pH) = 5.1885 - (1.2353 \times pH) + (0.0708 \times pH^2)$
60	$f(pH) = 1.836 - (0.1818 \times pH)$	$f(pH) = 15.444 - (6.1291 \times pH) + (0.8204 \times pH^2) - (0.0371 \times pH^3)$
80	$f(pH) = 2.6727 - (0.3636 \times pH)$	$f(pH) = 331.68 \times e^{(-1.2618 \times pH)}$

Table 4. pH effect function for higher temperature.

T	pH	$f(pH)$
90	$3.5 \leq pH < 4.57$	$f(pH) = 3.1355 - (0.4673 \times pH)$
90	$4.57 \leq pH \leq 5.62$	$f(pH) = 21254 \times e^{(-2.1811 \times pH)}$
90	$5.62 \leq pH \leq 6.5$	$f(pH) = 0.4014 - (0.0538 \times pH)$
120	$3.5 \leq pH < 4.3$	$f(pH) = 1.5375 - (0.125 \times pH)$
120	$4.3 \leq pH < 5$	$f(pH) = 5.9757 - (1.157 \times pH)$
120	$5 \leq pH \leq 6.5$	$f(pH) = 0.546125 - (0.071225 \times pH)$
150	$3.5 \leq pH < 3.8$	$f(pH) = 1$
150	$3.8 \leq pH < 5$	$f(pH) = 17.634 - (7.0945 \times pH) + (0.715 \times pH^2)$
150	$5 \leq pH \leq 6.5$	$f(pH) = 0.037$

The model calculates the mean shear stress (τ) on the walls of straight pipe sections at medium to high superficial velocities of either the liquid or gas velocities. This shear stress is used to calculate the corrosion rate in the pipe. If there are any obstacles or other geometrical changes in the flow, the shear stress will be higher than what is calculated by the computer program. Additionally, different flow regimes and obstacles may generate shear stress fluctuations where the shear stress peaks may be considerably higher than the average shear stress.

If the shear stress is high, this may cause mesa attacks, with corrosion rates significantly higher than what is estimated by the model [14].

$$\tau = 0.5 \times \rho_m \times f \times U_m^2 \quad (6)$$

In equations (6), f is friction factor, ρ_m mixture density (kg/m^3) U_m mixture velocity (m/s) [14]. In this study only one phase used, so no need to calculate mixture properties.

3. Results and Discussion

The data obtained from the experimental study was based on static conditions and also the shear stress was found by theoretical calculation in equation (6) by making some assumptions. In the mathematical modeling, the experimental conditions presented in Table 5 were taken into account.

Table 5. Test parameters in used NORSOK M 506 module.

Case	P_H	T (°C)	P_{CO_2} (bar)	V (m/s)
Case 1-8	4	20	1	2, 3, 4, 5, 6, 7, 10, 12
Case 9-16	5	20	1	2, 3, 4, 5, 6, 7, 10, 12
Case 17-24	6	20	1	2, 3, 4, 5, 6, 7, 10, 12
Case 25-32	4	50	1	2, 3, 4, 5, 6, 7, 10, 12
Case 33-40	4	80	1	2, 3, 4, 5, 6, 7, 10, 12

As a result of the theoretically calculated CO_2 corrosion rate, it is determined that 5.08 mm thinning would occur per year under these conditions. In the experiment, it is determined that corrosion rate would be 1.33 mm. However, NORSOK M 506 predicted four times higher for this case. Then the same calculations were repeated on 40 cases. The effects of flow rate, pH, and temperature on corrosion rate are explored in this section.

3.1 Effect of pH and flow rate

As mentioned earlier, in the experimental study all 40 cases were carried out with the assumption of the stable velocity. Then shear stresses were calculated according to this assumption. In this paper, the calculated shear stress values were used also for the mathematical modeling of CO_2 corrosion with NORSOK M 506 for comparison. To show flow rate and pH effects on corrosion rate, the researchers made measurements at different pH values. In Figure 2 the experimental study was compared with the mathematical model. The experimental results were shown in the dotted lines and the theoretical results were in the solid lines (Figure 2).

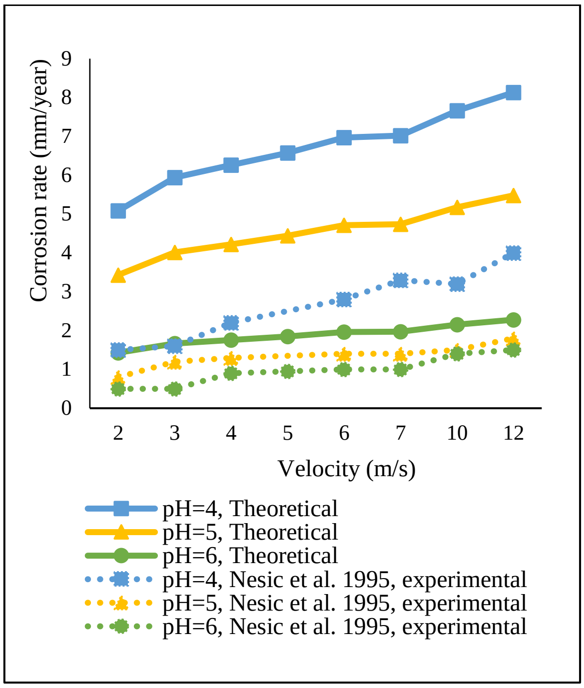

Figure 2. The effect of flow rate on corrosion rate at different pH values, comparison of values calculated with NORSOK, and experimental data from Nešić et al., 1995.
T=20 °C, P_{CO_2}= 1 bar, P_{total} =1 bar, pH=4.0-6.0, v=2-12 m/s.

As shown in Figure 2, the flow rate effect was greater in the mathematical model compared to the experiment. The same tendency was detected in the theoretical results also, the corrosion rate increased as the flow rate increased. This was more apparent at higher velocities, corrosion rate increased rapidly after flow rate v=7-12 m/s. However, this was the case when the solution pH was low. At higher pH values, the corrosion rate acceleration tendency was lower. The corrosion rate increased as the pH value decreased, but this increase was not rapid at high pH.

At high velocity conditions a more significant decrease is determined with increasing pH. In the mathematical model, as in the experiment, the fastest increase was observed at pH 4. While corrosion progresses rapidly to the metal surface during low pH, the corrosion rate decreases at moderate pH due to the partially protective feature of the protective film. At higher pH values, most minerals are insoluble and calcium carbonates build up on the surface and form a protective film, decreasing the corrosion rate [9], [13].

The theoretical results obtained with NORSOK M 506 were compared with the experimental results at v=2 and 4 m/s velocities for the effect of pH and velocity values at different temperatures (20 and

50°C). The results are given in Figure 3. There is no experimental data for pH=5 and 6 at temperatures 50 and 80°C. For this reason, at 50°C only theoretical results obtained from the NORSOK model were used in Figure 3. As expected, the values calculated with the NORSOK M 506 turned out to be higher when compared to the experimental data, the difference turns to be lower at high pH values, and temperature effects also decreased. As seen in Figure 3, the higher the pH value, the more consistent the experimental results of the NORSOK M 506 model. As expected the values calculated with the NORSOK M 506 turned out to be higher when compared to the experimental data, the difference turns to be lower at high pH values, and temperature effects also decreased. As seen in Figure 3, the higher the pH value, the more consistent the experimental results of the NORSOK M 506 model are.

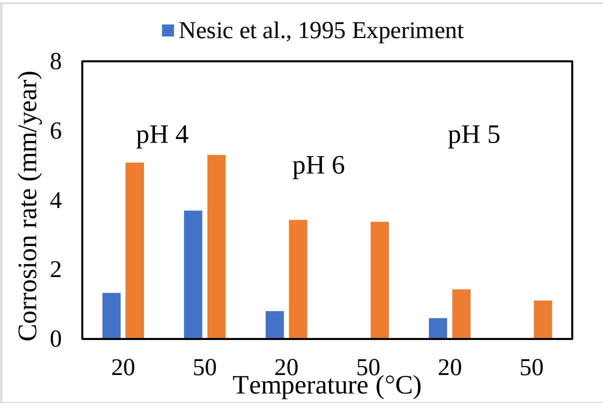

Figure 3. The variation of corrosion rate with pH at different temperatures, comparison of theoretical and experimental results from Nešić et al. 1995.
T =20, 50°C, P_{CO2} =1 bar, P_{total} =1 bar, pH=4.0-6.0, v=2, 4 m/s.

3.2 Effect of temperature

Since all physicochemical processes related to corrosion accelerate with temperature, the rate of corrosion increases with temperature [9], [13]. The rate of corrosion, increased as the temperature increased. Results are shown in Figure 4. The dots in solid lines are shown theoretical calculation, and the dots in dotted lines are shown experimental results.

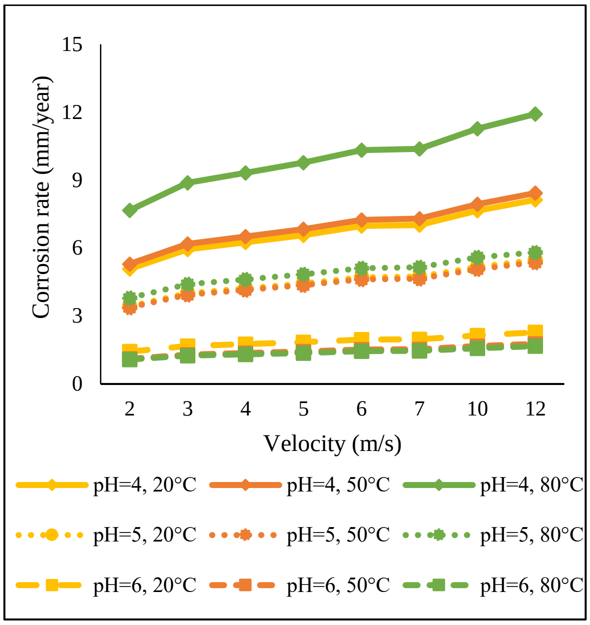

Figure 4. The effect of flow rate on corrosion rate, calculated by NORSOK, at different pH and temperature values.
T =20-80°C, P_{CO_2} = 1 bar, P_{total}=1 bar, pH=4.0-6.0, v=2-12 m/s.

As it is seen in Figure 4, the increase in corrosion rate is remarkable at high temperatures and low pH values in the mathematical model. In these conditions the effect of flow rate is more sensitive. At higher pH values, the effect of the flow rate decreased regardless of temperature. When corrosion rate is considered, although the effect of temperature was evident, the effect of pH is more dominant. After a 10 m/s flow rate, for a temperature of 20 and 80°C, pH 4, the increase in the corrosion rate is remarkable, but at pH 5 the difference between 20 and 80°C exceeding a flow rate of 10 m/s, was almost six-fold. Note that at high pH 6, the corrosion rate did not change much with temperature, while the effect of temperature increased as the pH decreased, however, the increase in the corrosion rate after 50°C was remarkable. Comparison with the model and the experimental study is shown in Figure 5. The effect of temperature was compared only at pH 4 because of a lack of experimental data. The dots in solid lines showed theoretical calculations, and the dots in dotted lines showed experimental results.

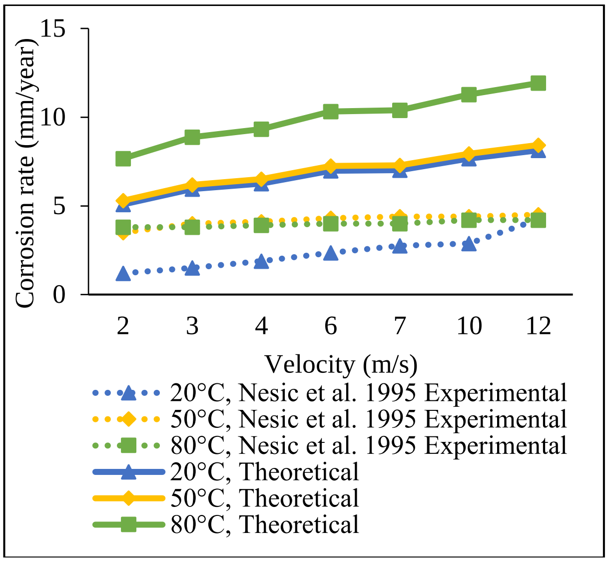

Figure 5. Comparison of theoretical results from NORSOK and experimental results from Nešić et al. 1995 about temperature effect on the rate of corrosion at various velocities.
T=20, 50, 80°C, P_{CO_2}=1 bar, P_{total}=1 bar, pH=4.0, v=2-12 m/s.

As seen in Figure 5, contrary to a sharp increase in corrosion rate at low temperatures in experimental study corrosion rate and flow rate increase with increasing temperature in the numerical model. And also the effect of the flow decreases at high temperatures in experimental study. In the NORSOK numerical model, the increase in corrosion rate with temperature has a higher acceleration after 50°C. For the determination of the difference between mathematical modeling and experimental study on CO_2 corrosion, a comparison was made using the cases given in Figure 6. T = 20°C, P_{CO2}=1 bar, P_{total} =1 bar, pH= 6.0, v=2-12 m/s.

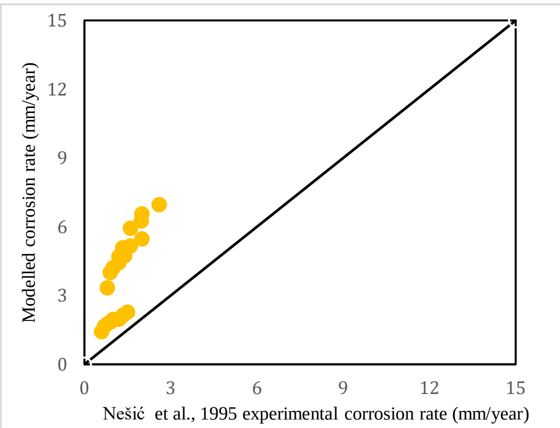

Figure 6. Comparison of the modeled corrosion rates by NORSOK with that obtained from Nešić et al., 1995 experimental study.

Although NORSOK M 506 shows a more conservative approach, except for extreme values the model has a moderately fit. At the extreme values of pH and temperature, there was a variance, however, it is acceptable because of the measurement errors in the experiment. As a result, the theoretical model has an acceptable correspondence reached and the differences are determined also more datasets could be produced in different conditions in comparison to the experimental study.

4. Conclusion and Suggestions

In this paper, the rate of CO_2 corrosion calculation was performed with the NORSOK M 506 model and the results are compared with the data collected with Nešić, Solvi and Enerhaug's (1995) experimental study and led to the following conclusions:

1. The flow rate effect was greater in the mathematical model compared to the experiment, and the corrosion rate increased as the flow rate increased. This was more apparent at higher velocities. Corrosion rate increased rapidly after flow rate v=7-12 m/s. However, this is the case when the solution pH is low. At higher pH, the corrosion rate acceleration tendency was lower.
2. At high velocity, a more significant decrease is determined with increasing pH. The fastest increase is observed at pH 4. While corrosion progresses rapidly to the metal surface during low pH, the corrosion rate decreases at moderate pH due to the partially protective feature of the protective film.
3. Experimental results at v=2 and 4 m/s velocities for the effect of pH and velocity values at different temperatures (20 and 50°C) are compared. As expected, the values calculated with the NORSOK M 506 turned out to be higher when compared to the experimental data. The higher the pH value, the more consistent the experimental results of the NORSOK M 506 model are.
4. At higher pH values, the effect of the flow rate decreased regardless of temperature. When corrosion rate is considered, although the effect of temperature was evident, the effect of pH is more dominant. After a 10 m/s flow rate, for a temperature of 20 and 80°C, pH 4, the increase in corrosion rate is remarkable, but at pH 5 the difference between 20 and 80°C exceeding a flow rate of 10 m/s, was almost six-fold.

In general, the level of corrosion rate increased with temperature and decreased with pH. Heating speeds up all the physicochemical processes causing corrosion and a lower pH indicates a higher concentration of corrosive H^+ ions. In extremes, like the lowest and highest temperature/pH combination, there is a certain variance. The NORSOK model is not tailored to suit a specific data set, but rather calibrated to optimum performance across a wide variety of operating parameters. Eliminating discrepancies is rather challenging. The researchers found that even tiny amounts of contamination steaming from contents are harmful and can lead to erroneous measurements. It was observed that there were contaminating metals on the sample surface at the experiment. It was discovered that the most serious contamination came from the rubber hose connecting the pumps to the lines, which is an active agent for corrosion inhibition. The performance of the NORSOK M 506 was therefore reasonable and in most cases acceptable and calculates nearly six times higher than experimental studies.

Contributions of the Authors

In the study carried out, Author 1 in the formation of the idea, design, and literature review, compilation, and interpretation of the results; Author 2 contributed to the evaluation, presentation, and analysis of the results obtained, in the titles of spelling and checking the article in terms of content.

Conflict of Interest Statement

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

There is no need for an ethics committee approval in the prepared article

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