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Simulation of CO_2 Corrosion of Carbon Steel in High Pressure and High Temperature Environment (HPHT)

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Abstract

In HPHT environments, the mechanism of CO_2 corrosion faces a challenge as an effect of chemical-physical reactions on the metal surface. The presence of other elements in the CO_2 system complicates corrosion behavior. To provide a realistic mechanism for corrosion process, some corrosion prediction models have developed software using fundamental theories such as electrochemical reactions and thermodynamics theories. Existing methods to predict corrosion rate models in HPHT environments have shown reasonable results. This paper reviews software of corrosion predictions which calculate corrosion rate based on mechanistic theories that study effects of H_2S, acetic acid (HAc) concentrations, shear stress, pH in temperature from 25°C – 100°C and pressure from 1–10 bar. From the simulation, corrosion rate increased significantly in the high pressure CO_2 environment. Corrosion rate at pH 4 increased to 30 mm/y at a temperature from 15°C to 90°C. While at pH 8 corrosion rate reached 4 mm/y. This lower corrosion rate indicated a tendency for deposits formation at higher pH. Corrosion rate behaves in a different mechanism at high temperatures. The corrosion rate decreased to 4 mm/y when the temperature increased to more than 90°C. Effects H_2S gas and HAc were identified to increase corrosion rate. Both elements provide extra cathodic reaction and create limiting current density in the cathodic reaction process based on polarization sweep models. However, the polarization graph calculated using corrosion models could not display passive behavior in the anodic polarization process. Thus, further, improvement should be considered. From the data calculation, it can be shown that corrosion prediction software can predict corrosion rate in HPHT conditions.

Keywords:
Carbon steel;
CO_2 corrosion;
High Pressure and High Temperature:
Mechanistic theories;
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INTRODUCTION

In oil and gas industries, CO_2 gas is considered the primary element that damages pipelines made of carbon steel. The gases can dissolve in the condensed water, which can reduce pH. Besides CO_2 gas, other elements such as H_2S gas and Acetic Acid (HAc) are also found in oil and gas environments in many reservoir areas [1-10]. Research on CO_2 corrosion models has been developed by researchers [3, 4, 5]. They focused on the effects of environmental and material factors on corrosion rates [9][10]. Initially, the main type of corrosion studied was uniform corrosion. It was generally believed that the significant factors governing corrosion rate were the concentration of CO_2 and temperature. However, a further study has shown that corrosion products such as film formation can contribute to the corrosion process [10]. After that period, models start to include the effects of scale formations in calculating corrosion rate [11].

Currently, models of corrosion rate have been more forward by considering complex factors involved in corrosion reactions, such as the effect of limiting current density, surface roughness, shear stress, thermos-chemical reaction, and water flow dynamics [14-23]. Combining existing elements cause corrosion process to occur in many ways and in several mechanisms. Understanding corrosion mechanism of those mixed elements requires reasonable corrosion models. Models for CO_2 corrosion have been developed through experiments and numerical theories [1-20].

In the form of semi-empirical correlations, researchers used electrochemical and thermodynamic theories, including iron dissolution, limiting current density, and activation reaction of dissolved ions. In HPHT environments, CO_2 corrosion faces a challenge as an effect of iron carbonate scales which can interfere corrosion rate. Furthermore, when H_2S is present in the CO_2 system, corrosion model will vary based on H_2S concentration [12, 14, 23, 27, 35].

Experimental studies performed by various authors [4, 21, 35] stated the effects of H_2S on cathodic and anodic processes and the formation of various crystalline forms of iron sulfide scales. Thus, the effect of H_2S gas on corrosion rate determined by its concentration. In addition, a weak acid, HAc, is also found to contribute corrosion rate. HAc concentration levels have been incorporated into the study as a key parameter [4, 8, 19, 20]. There are corrosion prediction models offered by industries that can be used to calculate carbon steel corrosion as discussed to accommodate these complex variables

MATERIAL AND METHOD

There are corrosion prediction models offered by industries that can be used to calculate carbon steel corrosion. Some of them will be discussed here.

NORSOK [28] standard is owned by the Norwegian Oil Industry Association and Federation of Norwegian Manufacturing Industries. The program only covers corrosion rate calculations 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 containing CO_2 at different temperatures, pH, CO_2 fugacities, wall shear stresses, and temperatures from 20 to160°C.

$$CR_t = K_t x fCO_2{}^{0.62} x (S/19)^{0.146+0.0324\log(fCO_2)} \\ xf(pH)t \tag{1}$$

Where C.R. is the corrosion rate (mm/yr), K_t is the constant for the temperature t, f CO_2 is the fugacity of the CO_2 (bar), S is Wall shear stress (Pa), *f(pH)t*is the pH factor at temperature.

Multicorp uses oil wetting and crude oil chemistry effects as parameters [25]. It contains an interface where the model developed by the institute for corrosion and multiphase technology, Ohio University's Research [25]. Wettability properties are based on the model published by Wang. [34]. Critical velocity for entraining free water by the flowing oil phase is used as the key variable. It also includes a phase inversion point and the flow pattern determination. Phase inversion calculations are based on the viscosities of the crude oil and water phases.

E.C.E. model considers the oil wetting correlation described in the equation based on field correlation. For low horizontal flow are used velocities < 1 m/s, the F_{oil} =1 [18]. The water cut is not important in influencing the actual corrosion rate at low velocities. E.C.E. program software calculates corrosion rate based on a method developed by de Waard and Milliams. The modified formula recommended was referring to C. de Waard, U. Lotz and A. Dugstad paper presentation [17]. They proposed a corrosion prediction expression as:

$$V_{cor} = \frac{1}{\frac{1}{V_r} + \frac{1}{V_m}} \tag{2}$$

Where V_r is corrosion reaction and V_m is mass transfer effect. The reaction corrosion is:

$$\log(V_r) = 4.84 - \frac{1119}{t+273} + 0.58\log\left(f_{CO_2}\right) \\ -0.34\ \left(pH_{act} - pH_{CO_2}\right) \tag{3}$$

And the mass transfer variable is defined as:

$$V_m = 2.8\frac{U^{0.8}}{d^{0.2}}\, fCO_2 \tag{4}$$

Where T is the temperature (^{0}C), pCO_2 is pressure (bar), $f(CO_2)$ is fugacity CO_2 (bar), $pHCO_2$ is the pH of pure water saturated with CO_2 at prevailing temperature and pressure. The fugacity of CO_2 is similar to its partial pressure but corrected for non-ideality of CO2 at high pressure and temperature. The mass transfer represents the main part of the dependence on flow velocity U and pipe diameter d.

Cassandra is a model to implement de Waard and B.P.'s experiences [15]. The input includes pH, CO_2 concentration, temperature, and water contaminant. This model does not consider a scaling temperature. The user must set an assumption of scaling temperature:

$$\log(V_r) = 5.8 - 1710/T + 0.67\log(P_{CO_2}) \tag{5}$$

RESULTS AND DISCUSSION

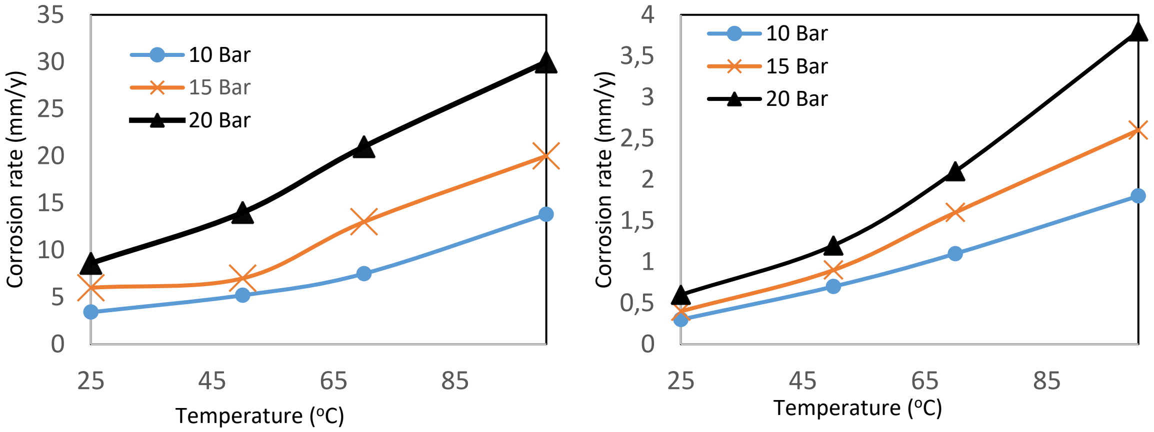
Prediction of CO_2 Corrosion Rate

Effect of pH on CO2 corrosion rate in HPHT environment

Effects of temperature and temperature on corrosion rate in CO_2gas environments are presented in Figure 1. As calculated by Cassandra, the effect of temperature varied from 25^{o}C to 90^{o}C. There was a clear acceleration of corrosion rates with increased temperature in both pH 4 and pH 8. The corrosion rate increased, at pH 4, to 20 mm/y in the range of temperature from 25 to 90^{o}c. At the same time, it increased 3 mm/y at pH 8 at the same range of temperature. Comparing effects of pH, corrosion rate reduced significantly at pH 8 compared to corrosion rate at pH 4. The low corrosion rate at pH 8 showed the formation of scale. These observations agree with some studies carried out in the past founding [16, 23, 26, 34, 35]. An increase in pH will cause the film to become thicker, denser and passivate anodic reaction.

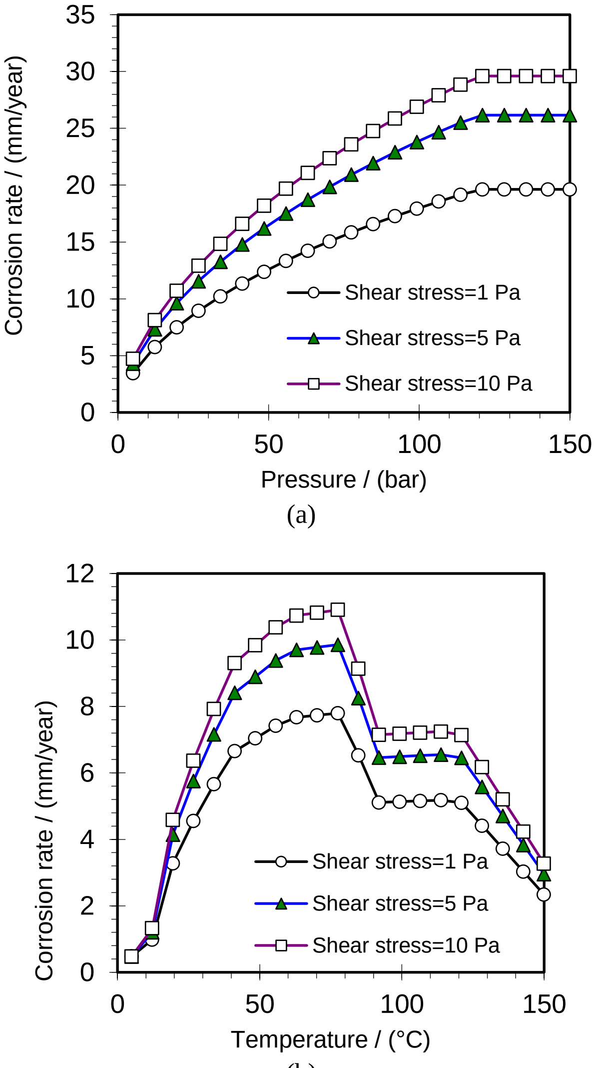
Effect of shear stress on CO_2 corrosion rate in HPHT environment

The corrosion rate of carbon steel at various shear stress, pressure and temperature are shown in Figure 2a and Figure 2b successively. At the temperature of 100^{o}C, pH 4 and saturated CO_2 gas at 10 bars, the corrosion rate increased when pressure and shear stress increased (Figure 2a). Similar trends were also seen at the pressure of 10 bar, pH 4 and saturated CO_2 (Figure 2b). In addition, the corrosion rate increased when shear stress increased. Investigators [23, 25, 26, 30, 31] explained that the effects of shear stress caused by fluid velocity on corrosion rate are associated with higher turbulence and mixing in the solution. Therefore, it affects the corrosion rate of the carbon steel surface and the iron carbonate film. However, temperature affects corrosion rate differently. At temperatures below 80^{o}C, hydrogen evolution acts as the rate determining step. At temperatures above 80°C, dense and protective films are produced to reduce corrosion rate.



(a) (b)

Figure 1. Corrosion rate at various temperatures and pressure at pH 4 (a), pH 8 (b) and saturated CO_2 gas as calculated by Cassandra [15]



(a)

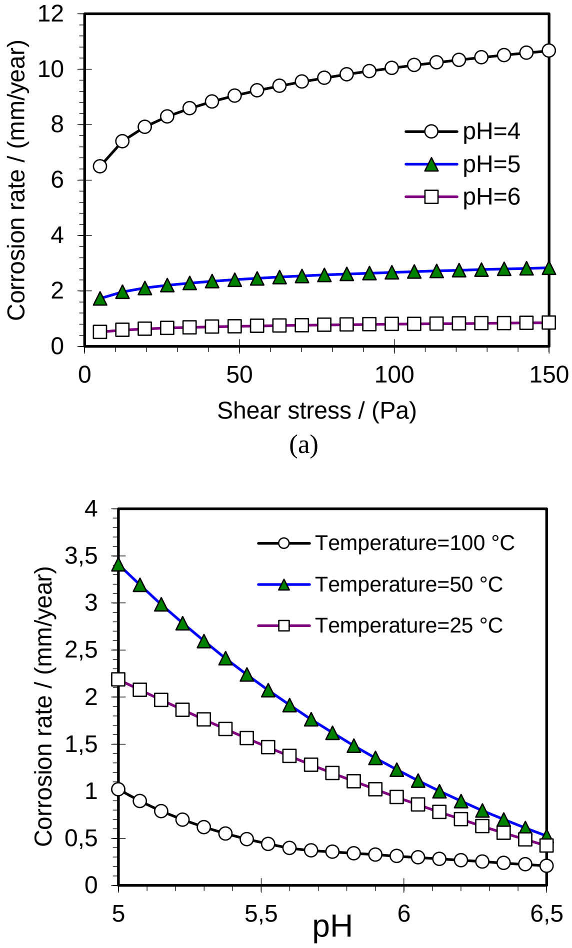
(b)

Figure 2. Effects of pressure (a) and temperature (b) on corrosion rate at varying shear stress as calculated by Norsok (CO_2 saturated solutions, 10 bar, pH4, and 100ºC) [28]

The effect of pH on the corrosion rate was studied in solutions saturated with CO_2 in the pH range from 4 to 6 (Figure 2a and Figure 2b). As the pH increases from 4 to 6, the anodic reaction rate increases, consistent with Bockris's iron dissolution mechanism [13]. This is expected since, with the increase of the pH, the concentration of the hydrogen ion decreases. In addition, the pH of wet gas in the CO_2 system is often assumed equal to the saturation of FeCO3 precipitation. Therefore, an increase in pH will cause the film to become thicker, denser and more protective.

Mechanistic Study of CO_2/H_2S Corrosion

The role of H_2S elemental is believed to influence corrosion rate. Figure 3 shows that increasing H_2S concentration causes higher cathodic polarization and corrosion potential. It was studied by Brown [14] that the effects of concentration of high H_2S in CO_2 will increase corrosion rate compared to a solution with a small concentration of H_2S. Kun-Lin was working with 10 ppm H_2S found that scale formed on the surface has a role in inhibiting corrosion rate. From the Figure 3, it can be seen that the corrosion rate is under charge-transfer control as an effect of H_2S concentration. The addition of H_2S also impacts diffusion limiting the current density of CO_2 corrosion.



(a)

(b)

Figure 3. Effects of shear tress (a) and pH (b) on corrosion rate at CO_2 saturated solutions as calculated by Norsok [28] (10 bar, 100°C (a) and (6 bar, 1 pa shear stress (b)).

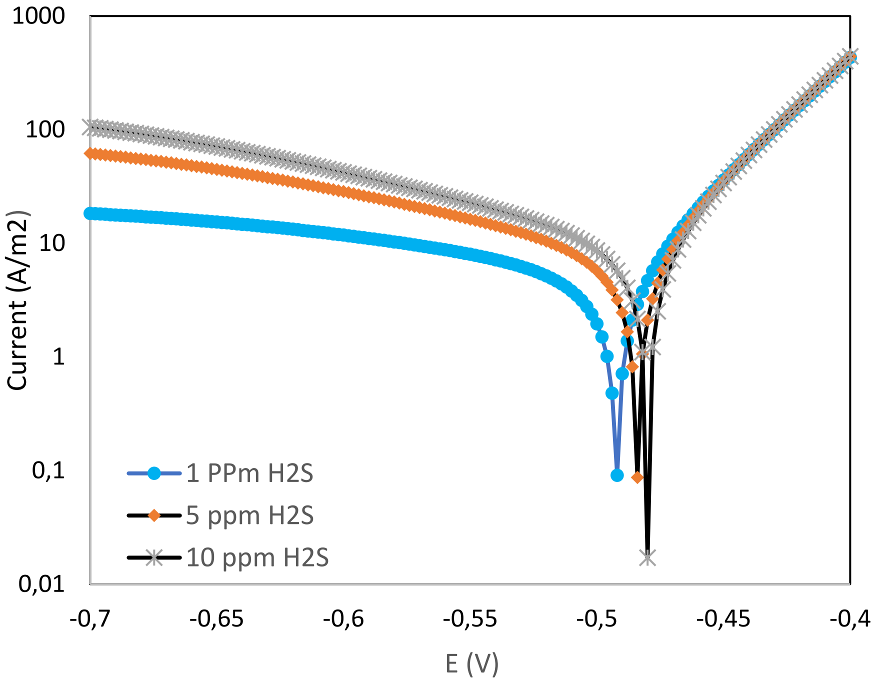


Figure 4. Potentiodynamic sweeps in 1 – 100 ppm H_2S, CO_2 saturated solution. at temp. 90_oC, pressure 10 bar, pH 4, stagnant as calculated by Freecorp [19]

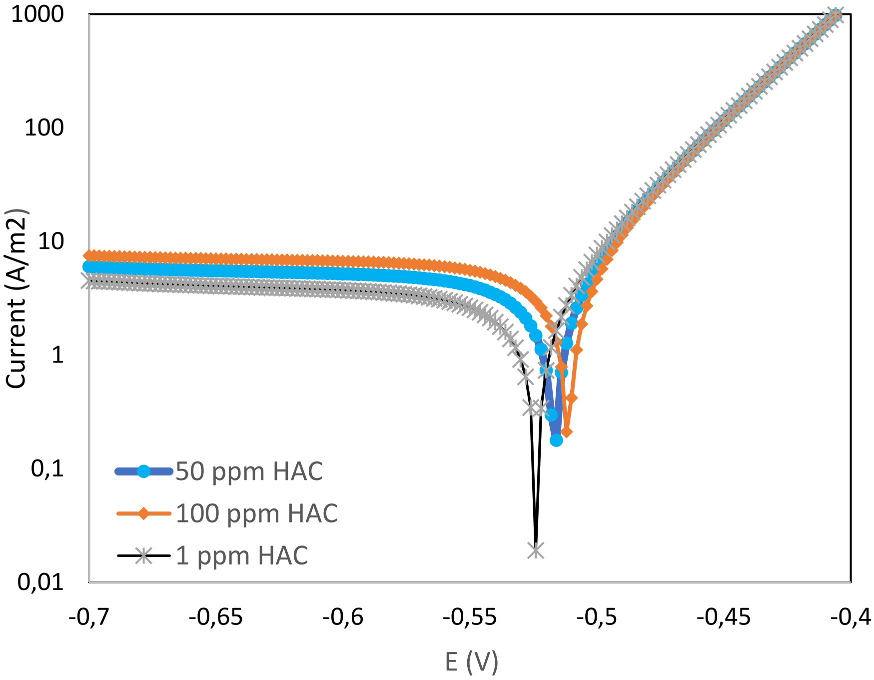


Figure 5. Potentiodynamic sweeps in 1 ppm HAc – 50 ppm HAc, CO_2 saturated solution. at temp. 90°C, pressure 10 bar, pH 4, stagnant as calculated by Freecorp [19]

Mechanistic Study of CO_2/HAc Corrosion

The other species, such as Acetic Acid (HAc) will also contribute to the corrosion rate. Studies [1-10, 26, 33, 34, 35, 36] have demonstrated that those multi-species factors can govern the corrosion process and in several mechanisms. The effect of HAc on the corrosion rate of carbon steel has been studied by many researchers [1-10, 23]. Figure 4 and Figure 5 present polarization sweep to research the effect of HAc on corrosion rate. Martin [23] pointed out that CO_2 induced acidification can also cause partial re-association of anions. Such weak acids, HAc can increase the oxidizing of H^+ by raising the limiting diffusion current for cathodic reduction. The presence of this acid also will tend to solubilise the dissolving iron ions [26]. The electrochemical behavior of carbon steel on the additions of HAc has shown that the presence of HAc in the solution decreases pH, increases the cathodic limiting current, and decreases Ecorr [23].

CONCLUSION

In general, all models confirmed that CO_2 caused a higher corrosion rate. Thus, in HPHT CO_2 environments, carbon steel is not recommended. With a pressure of more than 10 bar and a temperature of higher than 100°C, the corrosion was higher than 10 mm/y. The CO_2 corrosion process was accelerated with the presence of H_2S gas and HAc ions. H_2S and HAc have shown interferences in corrosion mechanism by facilitating limiting current density on cathodic reaction. Both elements also resulted in an extra cathodic reaction. In addition, shear stress increased corrosion rate through flow motion which impinged metal surface. In contrast with the effect of pH, pH catalyzed solution for film formation to retarded corrosion process.

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REFERENCES

[1] A. M. Anderko and R. D. Young, "Simulation of CO_2/H_2S Corrosion Using Thermodynamic and Electrochemical Models," *Corrosion*, NACE International, Texas, USA 1999, pp. 31

[2] B. A. Asma, Y. P. Asmara, and C. I. Mokhtar, "Study on the effect of surface finish on corrosion of carbon steel in CO_2 environment," *Journal of Applied Sciences*, vol. 11, no. 11, pp. 2053-2057, 2011, doi: 10.3923/jas.2011.2053.2057

[3] Y. P. Asmara, A. Juliawati, J. Jaafar, K. Azuar, J.P. Siregar, and T. Kurniawan, "Effects Pre-strain of Carbon Steel on Stress-Strain Diagram in CO_2 Environment with the Presence of H_2S," *International Journal of Material Science Innovations (IJMSI)*, vol. 2, no. 3, pp. 52-58, 2014

[4] Y. P. Asmara and M Ismail, "Study Combinations Effects of HAc in H2S/CO_2 Corrosion," *Journal of Applied Sciences*, vol. 11, no. 10, pp. 1821-1826, 2011, doi: 10.3923/jas.2011.1821.1826

[5] Y. P. Asmara and M. Che Ismail, "A Statistics Approach for the Prediction of CO_2 Corrosion in Mixed Acid Gases," *Corrosion and materials*, vol. 34, no. 4, pp. 25-30, 2009

[6] Y. P. Asmara, A. Juliawati, and A. Sulaiman, "Mechanistic model of stress corrosion cracking (scc) of carbon steel in acidic solution with the presence of H_2S," *IOP Conference Series: Materials Science and Engineering*, 2013

[7] Y. P. Asmara et al., "Application of response surface methodology method in designing corrosion inhibitor," *IOP. Conference Series: Materials Science and Engineering*, 2017.

[8] Y. P Asmara et al., "Predicting Effects of Corrosion Erosion of High Strength Steel Pipelines Elbow on CO_2-Acetic Acid (HAc) Solution," *IOP Conference Series: Materials Science and Engineering*, 2016.

[9] Y. P Asmara et al., "Effects Pre-strain of Carbon Steel on Stress-Strain Diagram in CO_2 Environment with the Presence of H2S," *International Journal of Material Science Innovations (IJMSI)*, vol. 2, no. 3, pp. 52-58, 2014

[10] Y. P Asmara et al., "Electrochemical Behaviour of High Stress Steel (AISI 4340) in CO2 Environments with the Presence of H2S Gas," *Applied Mechanics and Materials*, vol. 695, pp. 98-101, 2015

[11] Y. P Asmara et al et al., "Flow assisted erosion-corrosion of high-speed steel (H.S.S.) in nanofluid coolant," Applied Mechanics and Materials, vol. 695, pp. 143-146, 2014, doi: 10.4028/www.scientific.net/AMM.695.143

[12] Y. P Asmara, N.A.A. Razak, and Salwani, "Analysis of Corrosion Prediction Software for Detection Corrosion in Oil and Gas Environment Containing Acetic Acid, CO_2 and H2S Gases," *International Symposium on Corrosion & Materials Degradation (ISCMD 2014)*, 2014.

[13] J. O. Bockris, M. D. Drazic, and A. R. Despic, “The Electrode Kinetics of The Deposition and Dissolution of Iron,” vol. 4, pp. 325-361, 1961

[14] B. Brown, K. Lee, K. Nesic, “Corrosion in Multiphase Flow Containing Small Amount of H_2S,”, *Corrosion*, NACE International, vol. 3341, 2003.

[15] C. Cassandra and A. J. Mc Mohan, *B.P. Report*, no.1993, 220483, 1993.

[16] C. de Waard and U.Lotz, “Prediction of CO_2 Corrosion of Carbon Steel,” *Corrosion: NACE International, Houston*, vol. 69, 1993.

[17] C. de Waard and D. E. Milliam, “Carbonic Acid Corrosion of Mild Steel,” *Corrosion*, vol. 31,no. 5, pp. 131-135, 1975.

[18] NN, *Electronic Corrosion Engineer*, https://www.woodplc.com/solutions/expertise/a-z-list-of-our-expertise/software-and-products/ece-corrosion-and-materials-selectio, 2017

[19] FREECORP V1Technical Book, I.f.C.a.M.T., Ohio University Research Park, Athens, Ohio

[20] E. Gulbrandsen and K. Bilkova, “Solution Chemistry Effects on Corrosion of Carbon Steels in Presence of CO2 and Acetic Acid,” *Corrosion NACE International, Houston*, 2006, no. 6364

[21] K. J. Lee and S. Nešić, “Effect of trace amount of H2S on CO2 corrosion investigated by using the E.I.S. technique,” *Corrosion*, vol. 5630, 2005.

[22] K. Lee, “Mechanistic Modeling of CO2 Corrosion of Mild Steel in the Presence of H_2S,” *PhD Thesis*, Department of Chemical Engineering, Russ College of Engineering and Technology, Ohio University, 2004.

[23] C. F. Martin, “Prediction CO2 Corrosion with the Presence of Low concentration Acetic Acid in Turbulent Flow Conditions,” *Master Thesis*, Universitas Teknologi Petronas, 2009.

[24] M. Joosten, M. Achour, J. Kolts and J. Hembree, “Organic Acid Corrosion in Oil and Gas Production,” *Corrosion*, pp. 2294, 2002.

[25] NN, “Multicorp,” *Institute for Corrosion and Multiphase Technology*, Ohio University's Research and Enterprise Park.

[26] S. Nešić, “Key Issues Related to Modelling of Internal Corrosion of Oil and Gas Pipelines – A review,” *Corrosion Science*, vol. 49, no. 12, pp. 4308–4338, 2007, doi: 10.1016/j.corsci.2007.06.006

[27] B. a. Asma, Y. P. Asmara, and C. I. Mokhtar., “Study on the Effect of Surface Finish on Corrosion of Carbon Steel in CO2 Environment,” *Journal of Applied Sciences*, vol. 11, no. 11, pp. 2053-2057, 2011, doi: 10.3923/jas.2011.2053.2057

[28] NN, “CO_2 Corrosion Rate Calculation Model,” *Norsok Standard*, Norwegian Technology, Standards Institution, Oslo, Norway, 2005

[29] P. Wojnarowski, R. Czarnota, T. Włode, D. Janiga, J. Stopa1 and P. Kosowski, “The Possibility of CO2 Pipeline Transport for Enhanced Oil Recovery Project in Poland,” *MATEC Web of Conferences*, vol. 259, no. 5, ID: 01004, 2019, doi: 10.1051/matecconf/201925901004

[30] D. C. Silverman, “Rotating Cylinder Electrode - Geometry Relationships for Prediction of Velocity Sensitive Corrosion,” *Corrosion*, vol. 44, no. 1, pp. 42, 1988

[31] D. C. Silverman, “Simplified Equation for Simulating Velocity-Sensitive Corrosion in the Rotating Cylinder Electrode at Higher Reynolds Numbers,” *Corrosion*, vol. 59, no. 3, pp. 207, 2003

[32] A. Sutjipto, Y. P. Asmara, and M. Jusoh, “Behavior of MgO Based Ceramics under Electron Irradiation,” *Procedia Engineering*, vol. 170, pp. 88-92, 2017, doi: 10.1016/j.proeng.2017.03.017

[33] K. Videm, “The Effects of Some Environmental Variables on The Aqueous CO_2 Corrosion of Carbon Steel,” *The Institute of Material*, no. 13, 1994

[34] H. W. Wang, “CO_2 Corrosion Mechanistic Modeling in Horizontal Slug Flow,” *PhD Thesis*, Department of Chemical Engineering, Russ College of Engineering and Technology, Ohio University, 2002.

[35] S. N. Wei Sun, “Kinetics of Iron Sulfide and Mixed Iron Sulfide/Carbonate Scale Precipitation in CO_2/H_2S,” *PhD Thesis*, Department of Chemical Engineering, Russ College of Engineering and Technology, Ohio University, 2006.

[36] N. A. Abd Razak, Y. P Asmara and M. K. Kamaruzaman, “Influences of H_2SO_4 and NaCl concentrations on stress corrosion cracking of AISI 304 stainless steel,” *Advanced Materials Research*, vol. 893, pp. 410-414, 2014, doi: 10.4028/www.scientific.net/AMR.893.410