The Effect of Flow Rate and NaCl Concentration on the Corrosion Behavior of Carbon Steel in NaCl Solutions Containing H2S

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Abstract. Most of components in industry are made of carbon steel which has low corrosion resistance. Therefore, the industry’s equipment is highly susceptible to corrosion. This study is focused on the characterization of carbon steel corrosion in flowing NaCl solutions with H2S impurities. The corrosion rate was measured by using potentiostat. H2S gas was generated from the Kipp apparatus to produce a concentration of 600 ppm. The NaCl concentration was varied at 50, 40,000, and 60,000 ppm. The flow rate was varied at 0.5, 2.3 and 4.1 ft/s by utilizing a Rotating Disk Electrode (RDE). Corrosion mechanism was predicted by utilizing Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and confirmed by analysing the composition of the corrosion product using X-ray Diffraction (XRD), and Scanning Electron Microscope (SEM). The experimental results indicate that the breakaway velocity for NaCl solutions containing H2S of 600 ppm are around 4,500 rpm. At low level conductivity, corrosion rate increases as NaCl concentration increases. Then, after reaching 40,000 ppm, NaCl corrosion rate decreases along with the increase of NaCl concentration. The flow rate, NaCl concentration, and interaction between both variables are influential variable for corrosion rate. There is antagonistic influent to corrosion rate at 1000 rpm flow rate, 50 ppm NaCl, and 60,000 ppm NaCl.

Keywords: Carbon Steel; Corrosion; Flow Rate; Hydrogen Sulfide; Sodium Chloride

1. Introduction
Many industries commonly utilize carbon steel for equipment and piping material [1]. Carbon steel is a steel with carbon content up to 2.1%-wt., and it is still the main choice for equipment material in the chemical industry because of its strength and relatively low prices [2]. However, many streams in industries contain corrosive material such as NaCl and H2S that can damage carbon steel. The example of industries which produces corrosive fluids are: the chlor-alkali industry in which brine water containing chlorides up to 200,000 mg/L [3], oil and gas industry which produces water containing H2S with the concentration from 58.82 to 117.65 ppm [1], and geothermal industry in which gas containing H2S up to 600 ppm [4]. According to [5] and [6], the evaluation of carbon steel corrosion in chemical industry is essential in minimizing the costly economics and human losses due to corrosion.

It has been previously researched on that the corrosion rate increases along with the increasing flow rate in NACE brine solution by [7] while the effect of H2S concentration in 3% NaCl solutions had also been studied by [8]. However, [7] and [8] did not study the changes in corrosion rates when the differences between NaCl concentration and flow rates occur simultaneously. This phenomenon should be studied because in real applications, the flow rate and NaCl concentrations fluctuate. For example, in crude oil production, the older the well, the less oil produced and the more air produced. Consequently, the produced water flow rate would fluctuate, as well as the NaCl level. This variation might cause the new effect if there is the interaction between the variables (i.e. flow rate and concentration). Therefore, this study aims to determine the interaction effect between the NaCl concentration and the solution flow rate to the corrosion rate of carbon steel in H2S-containing NaCl
solutions. This research is essential for material selection or pretreatment that must be carried out by the chemical industry to maintain the pipe.

2. Methodology

The experiment begins with the preparation of a cylindrical API 5L carbon steel specimens from Panca Logam Store with the specifications of 3 mm in diameter and 2 cm in length. The specimens were then coated by Teflon, so that only one surface is in contact with the solution. Next, the specimen is mounted to the BASi® RDE (Rotating Disk Electrode) that stir the electrolyte solution to simulate the flow rate in piping industry. The electrolyte solution is a NaCl p.a. from Bratachem Store that is bubbled with H₂S gas 0.17 m³/s stoichiometrically produced by reacting Na₂S solids and HCl 1 M solution using the Kipp apparatus. The H₂S concentrations are determined by iodometric titration. H₂S concentration is set at 600 ppm to represent the most extreme conditions that might occur in the industry [4]. 1 M NaOH of 200 mL was prepared to capture excess H₂S. RDE is connected to a Gamry® Potentiostat type Reference 300w/ AE from Pennsylvania that would provide Cyclic Polarization (CP), Cyclic Voltammogram (CV), or Electrochemical Impendance Spectroscopy (EIS).

The main experiments consisted of corrosion rate measurement with CP. Then, the corrosion mechanism is predicted using electrochemical characterizations: CV and EIS without prior immersion. Physical characterization of the corrosion products is conducted by XRD and SEM.

The interaction between variables for all corrosion rates were measured using the full factorial design method with 95% confidence level for NaCl concentration and flow rate. The apparatus arrangement is shown in Figure 1.

![Figure 1](image)

To conduct XRD and SEM tests, 1 cm² plate carbon steel is immersed in a test solution. Immersion was carried out in the most extreme conditions (i.e. the highest NaCl concentration of 60,000 ppm). Pyrrhotite was discovered by [9] and [10] after immersing the carbon steel for 21 days. This experiment immersed the plate for 15 days for the XRD test and 27 days for the SEM test to observe the corrosion mechanism that occurred before and after the formation of pyrrhotite.

3. Result and Discussion

The corrosion rate of carbon steel in a NaCl solution containing H₂S was determined using the CP method. The NaCl concentration was varied at 50, 40,000, and 60,000 ppm to represent types of water: freshwater, seawater, and brine water. RDE rotation was varied at 1000, 4,500, and 8,000 rpm,
equivalent to 0.5, 2.3 and 4.1 ft/s successively to represent the whole regime: laminar, transitional and turbulent.

3.1. The Effect of Flow Rate
The effect of the flow rate on typical corrosion rates is shown in Figure 2. The corrosion rate data in Figure 2 shows that at the same H$_2$S concentration and NaCl concentration, the corrosion rate increases with increasing flow rate. The flow rate results in the change of the surface oxide film state due to an increase of fluid flow rate or surface shear stress [2]. This results in the unprotected metal from its oxide layer and direct contact with the electrolyte, thus the corrosion reaction occurs immediately.

![Breakaway velocity region](image)

**Figure 2.** The corrosion rate of carbon steel NaCl solution containing 600 ppm H$_2$S at various RDE flow rates

At a flow rate of 1000 rpm, the oxide layer damage is not significant to increases corrosion rate. The fluid flow rate at 4,500 rpm rotational speed will erode the protective layer on the metal surface so that the corrosion rate increases suddenly. Therefore, the breakaway velocity for H$_2$S-containing NaCl solutions is around 4,500 rpm. When the damaged protective layer is replaced by a new oxide layer such as at a rotating speed of 8,000 rpm, the increase in corrosion rate will slow down. This is consistent with changes in corrosion and erosion mechanisms as a function of fluid velocity according to [2] in figure 2.

3.2. The Effect of NaCl Concentration
The effect of NaCl concentration on the corrosion rate of carbon steel is shown in Figure 3. In general, the corrosion rate increases with increasing NaCl concentration from 50 ppm to 40,000 ppm. Initially the corrosion rate increases due to an increase in the conductivity of the solution. The conductivity value of the solution will increase with increasing NaCl concentration in the solution since NaCl is fully ionized in water. When the ions in the solution increase, transfer electron will be easier. This causes the corrosion reaction to occur more easily because a corrosion reaction involved electrons. Besides that, chloride ions can also dissolve the passive layer on the steel surface with a reaction shown in Equation (1) [2].

$$\text{FeOOH (passive layer)} + \text{Cl}^- \rightarrow \text{FeOCl (aq)} + \text{OH}^- \quad (1)$$

Then, the corrosion rate decreases with increasing NaCl concentration from 40,000 ppm to 60,000 ppm. At the same time, H$_2$S solubility decreases continuously with the addition of salt concentration and limits the rate of corrosion because the reduction of H$_2$S is a determinant of
the rate of reduction reaction [11]. The corrosion rate of carbon steel in all variation is shown in Table 1.

**Table 1.** The corrosion rate of carbon steel in all variation

| [H₂S] (ppm) | Flow rates (rpm) | [NaCl] (ppm) | I (A) | r (cm/s) | r (mm/y) |
|-------------|-----------------|--------------|-------|----------|----------|
| 600         | 1,000           | 50           | 3.93E-06 | 2.048E-09 | 0.6458   |
| 600         | 4,500           | 50           | 2.56E-05 | 1.334E-08 | 4.2069   |
| 600         | 8,000           | 50           | 3.45E-05 | 1.798E-08 | 5.6695   |
| 600         | 1,000           | 40,000       | 4.00E-05 | 2.080E-08 | 6.5730   |
| 600         | 4,500           | 40,000       | 4.93E-05 | 2.569E-08 | 8.1016   |
| 600         | 8,000           | 40,000       | 5.47E-05 | 2.850E-08 | 8.9890   |
| 600         | 1,000           | 60,000       | 2.00E-05 | 1.040E-08 | 3.2870   |
| 600         | 4,500           | 60,000       | 3.37E-05 | 1.756E-08 | 5.5380   |
| 600         | 8,000           | 60,000       | 4.40E-05 | 2.290E-08 | 7.2310   |

* r: corrosion rate

3.3. Interaction between NaCl Concentration and Flow Rate

The interactions between both variables were examined using data in table and the Experimental Design in the form of the Full Factorial Design method with confidence level 95%. Data from the statistic test is shown in Table 2. By comparing the P-value and uncertainty value in Table 2, it was found that the NaCl concentration, the flow rate, and the interaction between the flow rate and NaCl concentration are influential variables (P<0.05). The regression equation (2) is used to see the interactions between variables.

**Table 2.** Data from statistic test

| Source            | P.Value |
|-------------------|---------|
| [NaCl]            | 0.0001  |
| Flow rate         | 0.0001  |
| [NaCl]*Flow rate  | 0.0240  |
\[ r = 5.303 - 1.976 \text{ Flow} \_1000 + 0.348 \text{ Flow} \_4500 + 1.628 \text{ Flow} \_8000 - 1.971 \text{ NaCl} \_50 + 2.190 \text{ NaCl} \_40000 - 0.219 \text{ NaCl} \_60000 - 0.742 \text{ Flow}^{*}\text{NaCl} \_1000 \_50 + 0.728 \text{ Flow}^{*}\text{NaCl} \_1000 \_40000 + 0.015 \text{ Flow}^{*}\text{NaCl} \_1000 \_60000 + 0.316 \text{ Flow}^{*}\text{NaCl} \_4500 \_50 - 0.145 \text{ Flow}^{*}\text{NaCl} \_4500 \_40000 - 0.171 \text{ Flow}^{*}\text{NaCl} \_4500 \_60000 + 0.426 \text{ Flow}^{*}\text{NaCl} \_8000 \_50 - 0.582 \text{ Flow}^{*}\text{NaCl} \_8000 \_40000 + 0.157 \text{ Flow}^{*}\text{NaCl} \_8000 \_60000 \]

Equation (2) shows that when the regression coefficient of single variable is negative, the corrosion rate will decrease. Meanwhile, if the regression coefficient of single variable is positive, the corrosion rate will increase. This phenomenon is seen in Figure 2, at each flow rate variation, the corrosion rate at 40,000 ppm NaCl is the highest, which has positive regression coefficient. Furthermore, it can be seen that the corrosion rate at 50 ppm NaCl which has the negative regression coefficient is the smallest. Figure 3 shows that the lowest corrosion value is owned by the most negative coefficient variable, which is at a flow rate of 1000 rpm. 67% regression coefficient for interactions between variables is positive, this means that both variables are synergistic. Data from Figures 2 and 3 show that there is no antagonistic interaction between variables that reduce the corrosion rate.

3.4. Physical Characteristics and Electrochemical Characteristics
The mechanism of corrosion reactions that occur in NaCl solutions containing H₂S needs to be investigated to carry out appropriate control at each phase. The corrosion mechanism of carbon steel was investigated using physical characterization and electrochemical characterization.

The electrochemical characterization is conducted by Cyclic Voltammogram (CV) and Electrochemical Impedance Spectroscopy (EIS) without immersion. Typical voltammogram is shown in Figure 4. The voltammogram, in general, does not show a clear peak so that it can be guessed that only a single-stage cathodic reaction and anodic reaction happened. The shape of the curve indicates that the steel corrosion is a reversible reaction.

![Experiment data fitting](a)

![Experiment data fitting](b)
The corrosion mechanism of carbon steel was observed using Electrochemical Impedance Spectroscopy (EIS). The typical Nyquist plot and the imaginary structure of solution-oxide-metal interfaces and its equivalent electrical circuit as the fitting results of the Nyquist curve are shown in Figure 4.

The equivalent circuit obtained from fitting the Nyquist curve shows that the corrosion product consists of 2 layers. $R_u$ is indicated to be the electrical resistance of the solution. $R_{ox}$ is indicated to be the electrical resistance of electrolyte-corrosion product interphase, series of $R_p$ and $w$ are indicated as polarization resistance and Warburg element of mass transfer in Electrical Double Layer (EDL), while constant phase element $CPE_{dl}$ is indicated as EDL capacitance. The other Warburg element is indicated as mass transfer resistance in the corrosion product layer. This equivalent electrical circuit shows that corrosion products are porous because electrolytes can contact with the metal surface. The corrosion product is suspected as mackinawite which is a porous iron-sulfide compound on the surface of steel [12].

The physical characterization is conducted by X-Ray Diffraction (XRD) for 15 days of immersion and Scanning Electron Microscope (SEM) for 27 days of immersion. Corrosion products that are still attached to the carbon steel plate were analyzed using X-ray diffraction (XRD). The results of the analysis are shown in Figure 5. The peaks on the diffractogram indicate the presence of pyrrhotite (one of the iron-sulfide compounds).

Carbon steel specimen which has been immersed, cleaned, and analyzed using SEM to observe its corroded surface. The results of SEM analysis of carbon steel before and after corrosion at 120x and 1000x magnifications can be seen in Figure 6. SEM analysis has been continued with a larger magnification to find out the compounds found on the metal surface. Figure 6 shows that at 20,000x magnification, the surface of corroded steel shows a very similar image to pyrite morphology obtained by [13]. Pyrite is the most stable iron sulfide compound [14].
Figure 6. The physical characteristics Morphology of carbon steel surface before corrosion (a, c) and after corrosion (b, d) with 120x and 1000x magnification (e).

Pyrite morphology found using SEM at a magnification of 20,000x

3.5. Proposed Mechanism of Carbon Steel Corrosion in NaCl Solution Contains H₂S

Based on CV, XRD, EIS, and SEM data, the mechanism of carbon steel corrosion in H₂S-containing NaCl solution can be described by the following reactions. The anodic oxidation of iron in carbon steel can be written as reaction (3).

$$\text{Fe(s)} \rightleftharpoons \text{Fe}^{2+} + 2e^- \quad (3)$$

The electrons released from this reaction are then captured by H⁺ or H₂S and a cathodic reaction forms hydrogen gas as shown in reaction (4).

$$2\text{H}_2\text{S} + 2e^- \rightleftharpoons \text{H}_2\text{S}_2 + 2\text{H}^+ \quad (4)$$

In addition to the oxidation-reduction reaction, iron also reacts directly with H₂S which diffuses into the metal surface and is adsorbed to form the mackinawite corrosion product as presented in reaction (5).

$$\text{Fe} + (1-x) \text{H}_2\text{S} \rightleftharpoons \text{FeS}_m + (1-x) \text{H}_2\text{S}_2 \quad (5)$$

According to [15], iron in the solution can also form mackinawite as depicted in reaction (6).

$$\text{Fe} + \text{H}_2\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{FeSH}_\text{ads} + \text{H}_3\text{O}^+$$
$$\text{FeSH}_\text{ads} \rightleftharpoons \text{Fe(SH)}_\text{ads} + e^-$$
$$\text{FeSH}_\text{ads} \rightleftharpoons \text{Fe(SH)}_\text{ads} + e^-$$
$$\text{FeSH}_\text{ads} \rightleftharpoons \text{FeS}_m + x\text{SH}_- + (1-x)\text{H}_+ \quad (6)$$
Mackinawite is an unstable compound, so it further reacts with H₂S to produce pyrrhotite as indicated in reaction (7) [16].

\[
\text{FeS}_\text{m} + \text{H}_2\text{S} \rightleftharpoons \text{Fe(SH)}_\text{2} \rightleftharpoons \text{FeS}_\text{p} + \text{H}_2\text{S}_\text{p}
\]  

(7)

Mackinawite also has side reactions that form a complex compound that is soluble [17]. Complex formation and its dissociation reactions are shown in equations (8) and (9).

\[
\text{FeS}_\text{m} + \text{H}_2\text{S} \rightleftharpoons \text{Fe(HS)}_\text{2}
\]  

(8)

\[
\text{Fe(HS)}_\text{2} \rightleftharpoons \text{Fe(HS)}_\text{2}^- + \text{HS}^-
\]  

(9)

Finally, pyrrhotite turns into pyrite (FeS₂) as shown in reaction (10) [18].

\[
\text{FeS}_\text{p} + \text{H}_2\text{S} \rightarrow \text{[FeS–SH]}
\]  

\[
\text{[FeS–SH]} \rightarrow \text{[FeS₂–H₂]}
\]  

\[
\text{[FeS₂–H₂]} \rightarrow \text{FeS₂} + \text{H}_2
\]  

(10)

4. Conclusion

The corrosion rate of carbon steel in NaCl solution containing H₂S continues to increase with increasing flow rate. The breakaway velocity for NaCl solutions containing H₂S 600 ppm are around 4,500 rpm. At the low-level conductivity, corrosion rate increase with increasing NaCl concentration. Then, after reach 40,000 ppm NaCl concentration corrosion rate will decrease with increasing NaCl concentration. The flow rate, NaCl concentration, and interaction between both variables are influential variable for corrosion rate. There is antagonistic influent to corrosion rate at 1000 rpm flow rate, 50 ppm NaCl, and 60,000 ppm NaCl. The corrosion mechanism of carbon steel in NaCl solution containing H₂S begins with the oxidation of Fe to Fe²⁺ and reduction of H₂ to H₂, the formation of iron-sulfide compound started by mackinawite, then pyrrhotite and finally becomes pyrite.

5. References

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