CORROSION RATE OF CARBON STEEL FOR FLOWLINE AND PIPELINE AS TRANSMISSION PIPE IN NATURAL GAS PRODUCTION WITH CO₂ CONTENT

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Abstract

The purpose of this research is to investigate the corrosion rate of carbon steel as flowline and pipeline in natural gas production with CO_2 content. The influence of variety of conditions that represent the actual conditions in practice such as CO_2 partial pressure and solution composition, particularly NaCl percentage were performed. Research conducted by polarization test and simulation methods using PREDICTTM software. The result of this research is used to illustrate the level of corrosion rate of typical carbon steel i.e. API 5L X-52 occurred in natural gas pipelines due to the effect of dissolved CO_2 . From the experiments obtained that corrosion rate of steel in environments containing CO_2 ranged between 15-28 mpy. This high corrosion rate observed could severely damage natural gas transmission flowline and pipeline. The result of this research is the first step, as an input for prevention efforts, to prevent leakage of flowline and pipeline due to corrosion of CO_2 which appropriate with the lifetime that has been designed.

Abstrak

Laju Korosi Baja Karbon untuk Pipa Hulu dan Hilir sebagai Penyalur Produksi Gas Alam yang Mengandung Gas CO₂. Penelitian yang dilakukan bertujuan untuk mengkaji besaran laju korosi baja karbon yang digunakan sebagai pipa penyalur bagian hulu mapun hilir pada produksi gas alam yang mengandung CO₂. Beberapa parameter yang mewakili kondisi aktual di dalam praktek seperti tekanan parsial CO₂ beserta komposisi larutan, khususnya kadar NaCl ditunjukkan pengaruhnya. Pengujian dilakukan dengan metoda polarisasi dan simulasi dengan menggunakan perangkat lunak PREDICTTM. Hasil penelitian menggambarkan laju korosi baja karbon yang biasa digunakan sebagai pipa penyalur gas alam yaitu jenis API 5L X-52 sebagai pengaruh dari gas CO₂ yang terlarut. Berdasarkan hasil pengujian, diperoleh besaran laju korosi baja yang diperoleh ini merupakan nilai yang relatif tinggi sehingga dapat menimbulkan kerusakan yang signifikan terhadap pipa penyalur gas pada bagian hulu maupun hilir. Hasil penelitian merupakan langkah awal terhadap upaya pencegahan terjadinya kebocoran pada pipa penyalur akibat korosi oleh gas CO₂ agar umur pakai yang telah dirancang dapat dicapai.

Keywords: carbon steel, CO₂, corrosion rate, flowline, pipeline

1. Introduction

Nowadays, natural gas has become an alternative energy widely used in power plant in Indonesia. In years, the use of natural gas is increasing. This is supported by Indonesia's natural gas potential, which is quite abundant. However, the presence of natural gas in the earth cannot be separated from the water. Characteristic of Indonesian natural gas, with high CO_2 content, is often causing the failure of material by CO_2 corrosion process in the presence of water. From industrial review, the damage due to CO_2 corrosion usually occurs in materials of carbon and low alloy steels [1]. The use of steel often face problems related to corrosion, such as leakage due to the influence of CO_2 dissolved in water that cause corrosive environment (acidic). Though, this phenomenon is still not fully understood so that the research related to CO_2 corrosion still needs to be done to determine the corrosion mechanism of CO_2 [2]. In the pipeline, there is formation water (containing chloride ions) as a medium distributor and dissolved CO_2 that cause a uniform corrosion. Whereas, in the flowline often cause top of line corrosion problem because of the condensed water and dissolved CO_2 .

Internal corrosion due to dissolved CO_2 is commonly occurred in natural gas pipelines [3]. The content of formation water (containing chloride ions) and dissolved CO_2 can cause uniform corrosion in pipeline. At distribution of natural gas in pipeline, formation water is a distribution medium for natural gas produced from the wells. Therefore, a big concern must be given to formation water in controlling CO_2 corrosion.

Formation water as formation water medium contains dissolved salt with varies salinity [4]. The common salts contained are NaCl, CaCl₂, and MgCl₂. Variety of salt contained in formation water would also lead to differences in corrosion rate of material. In aerated formation water, difference in NaCl content will increase the corrosion rate up to 3.5% wt NaCl content [5]. Increasing NaCl concentration in the solution also increase the conductivity of the solution. However, this condition will affect the solubility of dissolved gases which act as reducing agent in the kinetics of corrosion processes which will affect steel corrosion rate on its environment.

Concentration of dissolved CO_2 , CO_2 partial pressure, chloride ion concentration and temperature are environmental parameter that could affect the corrosion rate of materials due to CO_2 corrosion. It is also influenced by the concentration of Fe^{2+} ion and fluid flow velocity [6-7]. These factors affect the terms of the reaction kinetics and the formation of protective layer which makes the corrosion rate caused by CO_2 becomes difficult to predict exactly. These parameters are very diverse and quite complex, therefore limitation must be taken to analyze corrosion rate of material due to these variables in more specific area.

In general, CO_2 corrosion is a very dangerous type of corrosion. CO_2 -contained atmosphere will be highly corrosive due to the reaction of CO_2 with water. This condition will lead to acidic environment which very corrosive [3]. The gas is dissolved in aqueous media, and form carbonic acid (H₂CO₃), which easily decomposed [8]. The compound decomposes by making the oxidation reaction becomes more and more, in that environment, which causes the corrosion rate becomes very high. This condition will certainly damage the flowline and pipeline, primarily will causes leaks in pipes which are not desirable in natural gas distribution applications.

In order to simulate the real condition of transmission gas pipeline, CO₂-saturated NaCl solution was used as formation water medium. Variation of NaCl concentration in this research was used as a variable to simulate the existing content of dissolved salts in a formation water medium of natural gas pipeline.

This research is focused and specified into the development of CO_2 corrosion rate model for carbon steel API 5L X-52 with CO_2 concentration up to maximum of 100 ppb, 1 atm CO_2 partial pressure, 25 °C in temperature, and 3.5% maximum of chloride ion content. The commonly used material for flowline and pipeline in oil and gas industry is carbon steel which comply with API 5 L X-52 specifications. A comprehensive conclusion is expected after a series of corrosion measurement test to gain the relationship of the effect of dissolved chloride ion concentration on corrosion rate of materials used in CO_2 environments.

2. Experiment

Corrosion rate measurement was performed using polarization method with a classical three-electrode cell glass setup. Reference electrode used was a standard calomel electrode with saturated KCl filling solution, while graphite acts as counter-electrode. Working electrode was API 5L X-52 steel with composition given in Table 1.

Corrosion rate of API 5L X-52 steel was examined under NaCl solution with two different environmental conditions. First condition was aerated environment and the other was in ambient CO_2 -saturated aqueous environments (Table 2).

Experiment was carried out by using Tafel analysis through polarization testing using $GAMRY^{TM}$ 5.06 software. Furthermore, the corrosion rate measurement of steel in CO₂ environments was also performed using PREDICTTM software.

Before conducting the experiment, steel sample was prepared according to standard for polarization testing method. API 5L X-52 steel is first cut to form a circle shape. The sample was then soldered with conductive cable, and the junction was embedded in epoxy resin to isolate the soldered area. Sample was grinded with grinding machine. The steel surface was grinded sequentially with 80, 150, 240, 400, and 600 grit carbide abrasive paper.

Table 1. Chemical Composition of API 5L X-52 Steel (wt %)

Fe	С	Si	Mn	Cr	Al	Ni	Co	Ti	Cu	Nb	V
99.07	0.14	0.011	0.662	0.0207	0.047	< 0.005	< 0.033	0.018	0.087	< 0.002	< 0.002

Table 2. Test Condition for Experiment

Parameters	Conditions
Electrode Material	API 5L X-52
Electrode Surface Area (cm2)	1 cm^2
T (°C)	25 °C
pH	4
pCO_2 (bar)	1
NaCl (ppm)	5000, 15000,
	25000, 35000
Electrochemical measurement Analysis	Tafel Analysis XRD
Tafel Analysis	-
Potential Range vc. Eoc (mV)	±250
Scan Rate (mV s-1)	0.5

In aerated NaCl solution, test was carried out under NaCl concentration of 5000-35000 ppm with watersaturated system. Open atmospheric condition was deliberately given to obtain aerated environment having an oxygen concentration in accordance with the concentration of NaCl in the solution. While testing under CO₂ environment, the NaCl solution was deaerated with CO₂ for at least 1 hour to reach pH 4 to represent the environmental pH on CO₂ corrosion. Temperature of the solution was also kept constant at 25 °C.

The corrosion products were also characterized using XRD analysis. The peak of each element is aimed to describe the chemical compound formed of the corroded steel surface.

3. Results and Discussion

Corrosion rate measurements in aerated NaCl environment (with no CO_2 content). Experimental results of corrosion measurement carbon steel in aerated environment are shown in Table 3.

Table 3 shows that the corrosion rate of steel increases with the increase of NaCl concentration. Increasing corrosion rate of carbon steel in aerated NaCl environment is affected by the conductivity of NaCl solution [4]. With increasing NaCl concentration in solution raise the conductivity of NaCl solution. This high conductivity enhances the corrosion current between the anode and cathode which will increase the corrosion rate of steel in the solution. However, highly dissolved salts in this solution will also reduce the great amount of dissolved oxygen which acts as producing agent [4]. Therefore, the corrosion rates of steel reach the maximum value at NaCl concentration 3.5% [4,9].

Corrosion rate measurements in CO₂-saturated NaCl environment. Testing under this condition represents the real condition of flowline and pipeline consisting of formation water medium and dissolved CO_2 . The results of this testing can be seen in Table 4.

 Table 3. Results of Corrosion Measurement of Carbon

 Steel in Aerated NaCl Environment

NaCl content (ppm)	E corr (mV)	I corr (µA/cm ²)	Corrosion rate (mpy)
5000	-364	6.822	3.789
15000	-434	14.57	6.659
25000	-398	20.49	9.363
35000	-406	25.52	11.66

 Table 4. Results of Analysis at the CO₂ Corrosion of Carbon Steel in CO₂-Saturated NaCl

NaCl content (ppm)	E corr (mV)	I corr (µA/cm ²)	Corrosion rate (mpy)
5000	-711	59.33	27.11
15000	-709	41.32	21.11
25000	-715	38.95	17.75
35000	-710	28.38	15.69

The increasing concentration of NaCl in the solution decreases the corrosion rate of steel in CO_2 environments. With increasing concentration of NaCl, the corrosion current density of steel is lowered, so that the corrosion rate of steel in this environment decreases. The result of this test reveals that increasing of NaCl concentration in solution up to 35000 ppm reduced the corrosion rate of carbon steel in CO_2 saturated NaCl environment.

Electrochemically, NaCl had an enormous effect on the kinetics of corrosion process. Initially, NaCl accelerated the corrosion process by accelerating the dissolution of metal which increased the anodic reaction [10]. Then, increasing NaCl concentration lowered the pH of the solution, thereby increasing activity of H^+ ions, indirectly accelerated corrosion kinetics [11-13]. Finally, increasing in NaCl concentration decreased the solubility of CO_2 which reduced the cathodic reaction [11].

The effect of NaCl regarding to the reducing of pH has been proven in this experiment. Increasing NaCl concentration has decreased the pH of NaCl solution containing saturated CO₂. However, pH was decreased with increasing NaCl concentration was not followed by increasing the corrosion rate of steel. It tends to decrease with the increasing of NaCl concentration.

Solubility of CO_2 is also affecting corrosion rate of carbon steel in NaCl solution containing CO_2 . Increasing the concentrations of dissolved NaCl in solution directly

reduced the solubility of CO_2 [11]. The solubility of CO_2 as function of NaCl solution is shown in Figure 1.

Regarding to effect of NaCl toward pH and solubility of CO_2 , it can be concluded that the solubility of CO_2 in NaCl solution tend to affect the kinetics of corrosion.

The decrease of the solubility of CO_2 in the solution directly reduces the cathodic reaction of corrosion. Cathodic reaction of CO_2 corrosion in this solution is shown in the following reaction [14].

$$CO_2 (gas) \leftrightarrow CO_2 (aq)$$
 (1)

$$\operatorname{CO}_2(\operatorname{aq}) + \operatorname{H}_2\operatorname{O} \checkmark 2\operatorname{H}_2\operatorname{CO}_3(\operatorname{aq})$$
 (2)

$$H_2CO_3(aq) + 2e^- \longrightarrow HCO_3^-(aq) + H_2(3)$$

$$2H+(aq)+2e^{-} \longrightarrow H_2(gas)$$
(4)

$$H_2O(l) + 2e^- \longrightarrow H_2(gas) + 2OH^-(aq)$$
 (5)

From above reaction, it can be seen at the first cathodic reaction in the kinetics of corrosion due to CO_2 . If the solubility of CO_2 decreases in electrolyte solution, it instantly reduces the rate of cathodic reaction that also affects the corrosion rate of steel in this environment [15].

Based on the above explanations, it can be inferred that decreasing corrosion rate of steel, with concentration 5000–35000 ppm of dissolved NaCl, caused by 2 main factors:

First, decreasing the solubility of CO_2 . Decreasing solubility of CO_2 in NaCl solution reduces the amount of reducing agent in this environment which resulting limited cathodic reactions rate on the surface of the metal. Inadequate of reducing agent and a decreasing of cathodic reactions rate on metal surfaces reduce corrosion rate of carbon steel in 5000–35000 ppm NaCl concentration under CO_2 -saturated condition.

Second, salt retarding factor. Salt retarding factor is characteristic of dissolved salt in solution that could inhibit anodic and cathodic reactions. Dissolved salt

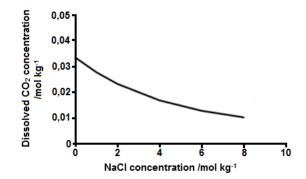


Figure 1. CO_2 Solubility as a Function of Salt Concentration at T = 25 °C, pH 4, and $pCO_2 = 0.97$ Bar [11]

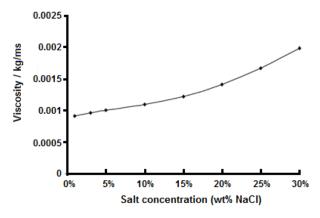


Figure 2. Effect of NaCl Concentration on Solution Viscosity [16]

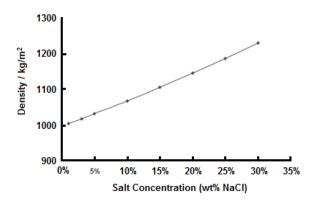


Figure 3. Effect of NaCl Concentration on the Density of the Solution [16]

content in a solution has affect viscosity and density of its solution. Increasing level of salt in a solution followed by increasing the viscosity and density of its solution [16]. Effect of dissolved salts on the viscosity and density of the solution can be seen in the Figure 2 and 3.

Increasing viscosity and density of the solution inhibit the mass transfer occurs in solution, as well as ion transfer. Dissolved salt in the NaCl solution impede mass transfer and charge transfer in the solution that inhibit the anodic and cathodic reaction [16]. This mechanism obviously explain decreasing corrosion rate of carbon steel in NaCl solution of 5000–35000 ppm under CO₂-saturated condition.

Corrosion rate measurement with PREDICTTM. PREDICTTM is software that represents the real environmental conditions accordance with applications in fields such as CO_2 partial pressure, temperature, and electrolyte composition. Corrosion rate simulation of carbon steel with various NaCl concentrations in solution containing CO_2 is shown in the Figure 4.

Based on the figure, it could be concluded that corrosion rate of steel, obtained from PREDICTTM software in CO²-saturated at 5000–35000 ppm NaCl, decreases with increasing of NaCl concentration. This result shows the same tendency as obtained from the polarization test in Table 4. The difference between laboratory testing and simulation by PREDICTTM software is believed due to corrosion product iron-carbonate formed on the surface. In the case of actual laboratory test, the decreased corrosion rate is affected by corrosion product formed which not considered in software simulation.

Characterization of the corroded surface. XRD test were carried out to analyze the corrosion product formed from the corroded steel surface which exposed in CO_{2} -saturated NaCl environment. XRD test result is shown in Figure 5.

XRD analysis of corrode steel surface show that the scale consist of FeCO₃. A peak near $30^0 2\theta$ is consistent with siderite (FeCO₃). FeCO₃ is the most important film that formed at carbon steel in sweet/CO₂ environment. This film can be function as a protective film for the carbon steel from the CO₂ corrosion. It is believed that the corrosion rate was decreased when this film formed as indicated shown in Table 4.

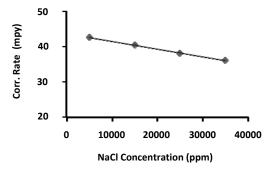


Figure 4. Steel Corrosion Rate from PREDICTTM Simulation Software

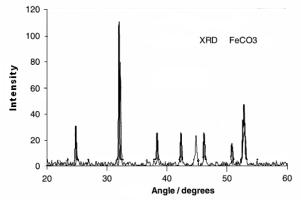


Figure 5. XRD Pattern of Corroded Steel Surface in CO₂-Saturated NaCl Environment

The film formation is strongly depending on the thermodynamics and kinetics of FeCO₃ precipitation. In principle, the precipitation process comprises two steps, nucleation and particle growth. With increasing pH, making the rate decreased solubility of FeCO₃ resulting high deposition rate [17]. The morphology of the film therefore depends on the dominating steps [18-19]. Protective film formation is accelerated by measures that restrict the transport of reaction products from the surface [20].

4. Conclusion

This research found that the increased of concentration of NaCl would decrease the corrosion rate at partial pressure of 1 atm and temperature of 25 °C. The primary corrosion product of steel is iron carbonate (FeCO₃) which could act as a protective film so that CO₂ corrosion rate can be reduced. Based on the experimental results, corrosion rate of API X-52 steel at 5000-35000 ppm NaCl in CO₂ saturated environment varied from 15 to 28 mpy (0.4–0.7 mm/year). This is categorized as fairly high which could endanger flowline and pipeline in natural gas production facilities where wall thinning process is severely occurred which tends to cause pipe leaks or failure. Therefore flowline and pipeline which subject to CO₂ corrosion need to be protected during in service.

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