

A Mechanistic Study on the Effect of Salt Concentration on Uniform Corrosion Rate of Pipeline Steel in Acidic Aqueous Environments

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ABSTRACT

CO₂/H₂S corrosion in oil and gas fields is often associated with acidity and salinity of fluids. However, the role of salinity is usually ignored in corrosion studies and corrosion prediction models. As part of a major project to model uniform CO₂/H₂S corrosion of carbon steel oil and gas pipelines in high salinity environments, the research reported herein investigated uniform CO₂ corrosion in high salinity acidic media. Experiments were carried out using a rotating disk electrode (RDE) in CO₂-saturated aqueous solutions at 10°C and a constant pH of 3.0, whilst varying NaCl concentration from 1 wt.% to 20 wt.%. The RDE setup was used because mass transfer of species to the surface in this setup is well understood. A low temperature was chosen to better distinguish between charge transfer and mass transfer-controlled reactions underlying the corrosion process. Surface analysis indicated that the corrosion process was uniform, and no corrosion layer formed on the steel surface. Both linear polarization resistance (LPR) and potentiodynamic polarization (PD) techniques showed a general decrease in the uniform corrosion rate with increasing salt concentration. The analysis of the PD sweeps showed that salt concentration did not influence the mechanism of anodic and cathodic reactions and the decrease in the corrosion rate was due to deceleration in the rate of both anodic and cathodic reactions. Modeling results showed that salt concentration mostly affected the rate of mass transfer of H⁺ ion to the surface by changing H⁺ diffusion coefficient and H⁺ activity coefficient.

Keywords: Uniform CO₂ corrosion, salt concentration, salinity, non-ideal solutions, rotating disk electrode (RDE), produced water

INTRODUCTION

Dissolved salts are generally present in water produced during hydrocarbon production from underground reservoirs.¹ It is reported that, in the USA, the concentration of salts (i.e. salinity) in water produced from conventional hydrocarbon reservoirs can vary from 1000 mg/l (~0.1 wt.%) to 400,000 mg/l (~28 wt.%).² In addition to salts, dissolved corrosive gases (CO₂ and H₂S) are present in produced water, which make the mixture a complex corrosive environment for metallic parts and equipment used throughout the production process.

Internal CO₂ corrosion of carbon steel tubulars is a common type of corrosion that occurs in the oil and gas industry.³ A large body of research exists on CO₂ corrosion. However, most of this research has been focused on low salt concentrations ranging from 1 to 3 wt.%, which is often much lower than what is usually encountered in the field.⁴ There are few studies on uniform CO₂ corrosion at salt concentrations above 3 wt.%. In recent comprehensive work reported by Madani Sani *et al.*⁵ the uniform CO₂ corrosion rate of carbon steel reached a maximum between 1 wt.% to 3 wt.% NaCl and then decreased continuously by further increase in NaCl concentration. The decrease in the corrosion rate was attributed to the retardation of both anodic and cathodic reactions. Similar results have been published by Eliyan, *et al.*^{6,7}, and Liu, *et al.*⁸ However, Fang³, Zeng, *et al.*⁹, and Han, *et al.*¹⁰ who reported a continuous declining trend in the rate of uniform CO₂ corrosion of carbon steel with increasing NaCl concentration.

This work, as a small part of a large ongoing joint-industrial project (JIP) focused on corrosion mechanisms related to the internal CO₂/H₂S corrosion of pipeline-grade carbon steel, covers the effect of salt concentration on uniform CO₂ corrosion in acidic media. The data presented in this article will be used in development of a corrosion-rate-prediction model as one of the final goals of the JIP.

In this paper, the effect of NaCl concentration on corrosion behavior of X65 carbon steel was investigated by performing electrochemical experiments in CO₂-saturated aqueous solutions with different NaCl concentrations (1 wt.% to 20 wt.%) at 10°C, 1 bar total pressure and pH 3.

EXPERIMENTAL PROCEDURE

Setup and apparatus

Figure 1 shows the experimental apparatus. Experiments were carried out in a custom-made glass cell with an outer jacket for temperature control. An industrial chiller (not visible in Figure 1) was used to circulate glycol (the green liquid in Figure 1) through the outer jacket for controlling the solution temperature during the experiments. Glycol did not have any contact with the experimental solution.

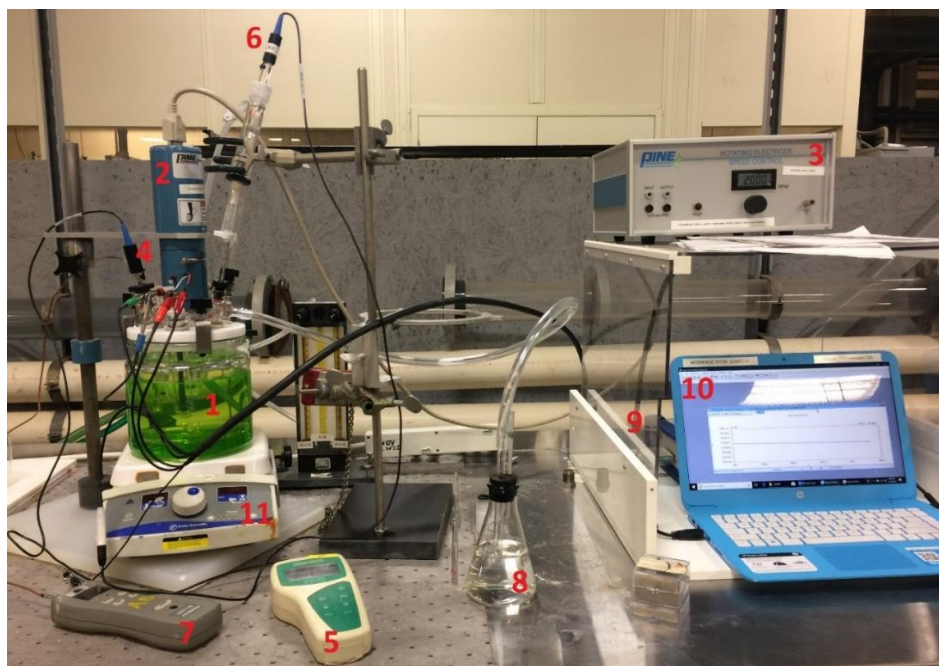


Figure 1. The experimental apparatus: (1) glass cell, (2) motor, (3) rotation speed controller, (4) pH probe, (5) pH meter, (6) Ag/AgCl reference electrode, (7) thermometer, (8) gas out bubbler, (9) potentiostat for data acquisition, (10) laptop for data collection, (11) hot plate stirrer.

Figure 2 shows a close-up view of the glass cell. A conventional three-electrode setup was used for the experiments that included a rotating disk electrode (RDE) assembly as the working electrode, a graphite bar as the counter electrode and an Ag/AgCl electrode as the reference electrode. The counter electrode was mounted in a glass tube with a porous tip to avoid interference of species (such as H_2 and O_2) that form on the counter electrode during the potential sweep, with the corrosion process. The porous tip provides ionic conductivity between the counter electrode and the solution. The reference electrode was placed in a Luggin capillary that was filled with 1M KCl. The capillary tip was adjusted close to the RDE almost at the same level to diminish the effect of solution resistance on the electrochemical measurements, but, not too close to disturb the RDE laminar flow (approximately 3 mm from the Teflon RDE holder). The immersion depth for the RDE was in the middle of the glass cell. However, it is reported that the RDE immersion depth does not influence the electrochemical measurements.¹¹



Figure 2. A picture of the custom-made glass cell and its components used in the RDE electrochemical experiments: (1) glass cell, (2) outer jacket, (3) Teflon lid, (4) clamp, (5) coolant (glycol) in, (6) coolant out, (7) RDE and its holder, (8) pH probe, (9) Luggin capillary for the Ref. electrode, (10) counter electrode, (11) thermocouple, and (12) magnetic stirring bar.

RDE Specimen

The RDE specimen was a carbon steel cylinder with a diameter of 5 mm and a height of 4 mm. The specimen was flush mounted in a Teflon holder as shown in Figure 3. The assembly was polished before each experiment. The two red O-rings were used to seal the connection between the specimen holder and the RDE shaft.



Figure 3. (a) The bottom view of the RDE specimen flush mounted in a Teflon holder, (b) The side view of the specimen holder.

Material

The carbon steel grade used for the experiments was API 5L X65, a common steel grade for oil and gas transmission pipelines.¹² Table 1 shows the chemical composition of the experimental steel. The carbon steel microstructure (not shown here) was uniform, fine structure of pearlite in a ferrite matrix.

Table 1: Chemical composition of the experimental carbon steel (API 5L X65) (in wt.%).

Al	As	C	Co	Cr	Cu	Mn	Mo	Nb	Ni
0.028	0.008	0.05	<0.001	0.252	0.173	1.51	0.092	0.034	0.291
P	S	Sb	Si	Sn	Ti	V	Zr	Fe	
0.004	<0.001	<0.001	0.167	0.002	0.012	0.04	<0.001	balance	

Electrochemical measurements

Experiments were conducted in CO₂-saturated aqueous solutions with different NaCl concentrations to investigate the effect of salt concentration on uniform CO₂ corrosion. NaCl is the major salt present in water produced from conventional hydrocarbon reservoirs;¹³ thereby, it was chosen for the present study. A low solution temperature of 10°C was chosen for the experiments. Lower temperatures slow down the kinetics of the electrochemical reactions at the metal surface more than the rate of diffusion of electroactive species to the metal surface. This results in more separation between the charge transfer and the mass transfer-controlled regions of the cathodic potentiodynamic sweeps and facilitates evaluation of the effect of salt concentration on each region. Even though it has been shown that corrosion due to the presence of 1 bar CO₂ is not dominant at pH lower than 4¹⁴, experiments were conducted in an acidic medium of pH 3 to broaden the range of data required for developing a CO₂ corrosion prediction model at high ionic strength.

For each experiment, NaCl was dissolved in one liter of deionized water (18 MΩ.cm) in the glass cell. The solution was then sparged with CO₂ for at least 2 h, while being stirred. After about 1 h of sparging, pH of solution reached to a stable value (Table 2). At this point, pH was adjusted to 3.0 by adding 0.1 M HCl to the solution. More HCl was required for low NaCl concentrations. The specimen assembly (shown in Figure 3) was sequentially wet polished with 240-, 400- and 600-grit abrasive papers. Subsequently, the assembly was ultrasonically degreased with isopropanol for 3 min and dried in cool N₂ gas prior to immersion in the test solution.

Table 2. The autogenous pH of CO₂-saturated aqueous solutions for different NaCl concentrations at 10°C and 1 bar total pressure.

NaCl concentration (wt.%)	1	3	10	20
Avg. autogenous pH	3.83	3.75	3.61	3.45

After introducing the RDE assembly to the solution and prior to each electrochemical test, the open circuit potential (OCP) was monitored until a stable potential value ($\Delta E_{OCP} < 2$ mV/min) was achieved. The linear polarization resistance (LPR) technique was performed to measure the corrosion rate. Electrochemical impedance spectroscopy (EIS) was carried out to determine the solution resistance (*iR* drop). Potentiodynamic polarization (PD) was done to study the effect of salt concentration on the mechanism of uniform CO₂ corrosion. A Gamry Reference 600[†] potentiostat was used for all the electrochemical measurements. Table 3 and Table 4 summarize the conditions and the methods used in the experiments. Each test was repeated two times in order to check the reproducibility of results.

[†] Trade name

Table 3. The experimental conditions for studying the effect of salt concentration on uniform CO₂ corrosion of carbon steel.

Parameter	Description
Specimen material	X65 carbon steel
RDE diameter (mm)	5.00 ± 0.05
Temperature (°C)	10.0 ± 0.5
Total pressure (bar)	1
CO ₂ partial pressure (bar)	0.97
NaCl concentration (wt.%)	1, 3, 10 and 20
pH	3.00 ± 0.02
RDE rotational speed (rpm)	2000 ± 2

Table 4. The experimental methods for studying the effect of salt concentration on uniform CO₂ corrosion of carbon steel.

Method	Description
Potentiodynamic polarization • Potential range (V vs. OCP) • Scan rate (mV/s)	-1.0 to 0.2 0.5
Linear polarization resistance • Potential range (mV vs. OCP) • Scan rate (mV/s)	-5.0 to 5.0 0.125
Electrochemical impedance spectroscopy • Frequency range (Hz) • DC voltage (V vs. OCP) • Peak to peak amplitude (mV) • Sampling rate (points/decade)	10,000 to 0.1 Zero 10 8

Experimental considerations

1. The level of dissolved oxygen, monitored by an Orbisphere[†] 410 oxygen meter at the gas outlet, was kept less than 10 ppb during the experiments.
2. Temperature could not be kept constant by just circulating coolant in the glass cell jacket. Therefore, a hot plate was used continuously to balance the temperature. A constant temperature of 10 ± 0.5 °C was achieved by an equilibrium between coolant circulation and the hot plate.
3. Measuring pH correctly in solutions with high salinity is challenging.¹⁵ The pH measurements were done with a double-junction pH probe, which was resistant to Na⁺ ion interference.
4. At low NaCl concentrations, H₂ gas bubbles formed on the surface of the RDE in the cathodic potentials and caused spikes in the PD sweeps as seen in Figure 5.
5. Since there was no significant difference in the PD sweeps for scan rates of 0.125 mV/s and 0.5 mV/s, the latter was chosen for PD experiments.
6. Figure 4 compares the cathodic sweeps at the two scan rates for 20 wt.% NaCl.