Evaluation the Corrosion of Mild Steel Rings in Simulated Conditions of Natural Gas Transportation

Jewad K. Shneine

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq.
Corresponding Author: jkshneine@gmail.com.

Abstract

   Corrosion of steel rings (steel tubes) under natural gas production conditions has been studied in a 2 L glass autoclave. Steel tubes, axially constructed with cavities of aspect ratios 3×1 mm, were exposed to CO_2 saturated chloride salt solutions in a glass autoclave for 4 days at a flow rate of 6m/s and CO_2 flow of 5 bar. Effect of temperature, chloride ion concentration, and inhibitor ratio has been studied. Accordingly, removal mass, surface layer mass and the corrosion rate were evaluated at different conditions. Fe^{2+} concentrations and pH values were also evaluated. The corrosion degree of the tested samples is assessed by polarizing microscope at different magnification values. Results showed that high corrosion rates affected by high temperatures and high chloride concentrations, have been particularly reduced by addition of Dodisclae V3962 inhibitor. Formation of a fixed surface layer mass might be the reason for the high corrosion inhibition.
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Introduction

   Corrosion of mild steel under CO_2 containing salt solutions is considered as a serious problem in natural gas pipe lines [1,2]. This might be caused by electrochemical and hydrodynamic effects [3]. The magnitude of this kind of corrosion would be especially greater in presence of flow hindrances. Compared to smooth surfaces, corrosion under flow hindrances can be increased to threefold. The flow induced corrosion of mild steel in CO_2 saturated and O_2 free aqueous solutions can be described by the following equation:

$$Fe + 2\,CO_2 + 2\,H_2O \longrightarrow Fe + 2\,H_2CO_3 \longrightarrow Fe^{3+} + 2HCO_3^- + H_2$$
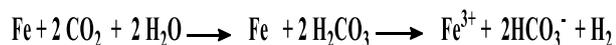
   Whether it comes to local corrosion or simply to a generally, uniform removal, or to what extent the expected corrosion rates lie, depends on the following factors: Reaction temperature, Composition of medium, pH value of the medium, and the Flow rate [3].

   Particularly in the case of flow disturbances due to discontinuities, e.g. cavities, there is an increased corrosion effect of the material. Therefore, it is necessary to investigate the flow conditions at surface disturbances [4,5]. The main objective of the present work is to investigate the effect of the ratio of two commercial inhibitors on the corrosion rate of steel rings with cavities under different temperatures and salt concentrations.

Experimental Work
Chemicals

   The following chemicals: sodium acetate buffer, 1, 10-phenanthrolium chloride solution, hydroxyl ammonium chloride solution, hydrochloric acid**,** sodium hydroxide, sodium chloride, calcium chloride, calcium hydroxide, petroleum ether, and ferrous chloride were provided from Aldrich company of analytical grade.

   The following Inhibitors were used in this work:

1. *Dodigen 481* [6]: this is a naphthenic acid imidazoline corrosive inhibitor, brown or red-brown viscous liquid, soluble in gasoline, diesel oil, alcohols, amines and organic acids and insoluble in water. It can be obtained from condensation of Naphthenic acid and ethylenediamine or diethylene triamine or other amines.
2. *Dodiscale V 3962* [7]: this is a polyethylenepolyamine-N-methylphosphonic acid (anionic type inhibitor from the class of organic phosphates). Both inhibitors were provided from Yi Wang Shanghai Sunwise Chemical Co., Ltd.

Instruments

1- Glass autoclave

The glass autoclave was used to carry out the tests can withstand pressures of up to 12 bar and temperatures up to 200°C. The 1.7 L autoclave which provided from Büchi/ Germany, was heated with a heating agent triethylene glycol (TEG) via a double jacket. The oil was circulated through a thermostat, where it was cooled, if necessary. The CO_2 gas was pumped into the autoclave via an appropriate device on the autoclave cover.

2- pH meter

pH measurements accomplished using Metrohm international pH meter.

3- A Spectrophotometer DR Lange Photometer LP3W, Germany, was used to determine Fe^{2+} concentration of the experiment.

4- Polarizing Microscope

Determination of the strength and type of corrosion was carried out using a polarizing microscope provided from Olympus Corporation.

Sample material (mild steel ring)

40 mm length pipe sections were cut from 2 3/8 pipe of the material 38/Mn5/C75 and designed to an outer diameter of 68/2 mm. The surface area was 163.2 cm^2: 86 cm^2 outside; and 77,2 cm^2 inside. The sample was provided with axially milled cavities of dimensions (W×H): in (3mm×1mm). In each case two identical cavities being opposed in such a way that the sample showed no imbalance (Fig.(1)) [4].
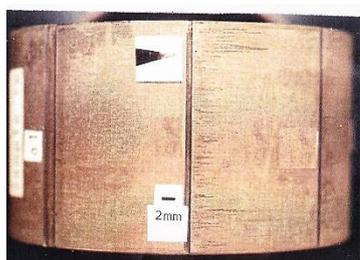
Fig.(1): Tested sample material with cavities used in the corrosion experiments.

Pre-treatment of Mild steel ring

Firstly the metal ring was rinsed with petroleum ether in ultrasonic bath for 10 minutes, then with acetone for further 10 minutes and finally with tap water for 1 minute. The mild steel ring was rinsed with hydrochloric acid (10%) for 10 minutes, then with tap water for 1 minute. The sample was gently scrubbed with quartz sand to achieve a uniform appearance. Then it was rinsed with tap water, then again with hydrochloric acid (10%) for 5 minutes in ultrasonic, with 0.1 M sodium hydroxide solution, with tap water for 5 minutes, distilled water, and rinsed 1 minute with methanol. Then, the sample was air-dried and weighed which was considered the mass of the sample before the experiment (m_1).

Experimental media procedure

According to a simplified version of conditions dominated in natural gas transportation, two different chloride salt solutions were prepared [4,5]. 251.89 g (2.535 mol) of sodium chloride and 237.74 g (2.140 mol) calcium chloride were dissolved in 1.7 L of distilled water. The total chloride content of the first solution was 180 g/ L, in which the molar ratio of the Na/ Ca being 2:1. Alternatively, a solution with 0.6 mol/L NaCl concentration was prepared. So 1,00 g (0.017 mol) of sodium chloride was dissolved in 1.7L of distilled water. Both solutions were adjusted to pH = 7 using 0.1 M sodium hydroxide solution. The 2L bottle solution was evacuated three times for 30 min each with a water jet pump with stirring. The solution was then saturated with CO_2 gas.

Corrosion experimental procedure

The mild steel ring was firstly incorporated into the poly tetraflouro ethylene (PTFE) fixture, without touching the surface, which was then mounted on a stirrer shaft of the 2-Liter Büchi autoclave. The flow breaker was adjusted in such a way that a uniform flow was formed axially to the ring. Then, the autoclave was closed by placing the lid on the glass head and screwing it on.

The contents were then evacuated by pressurizing CO_2 to 5 bar three times. In the course of the flow of CO_2, the thermo element neck was removed. To compensate the increased pressure during the heating up at the beginning of the experiment, the autoclave was fed with CO_2 pressure of 2-3 bar. After the heating phase, a pressure of approximately 5 bar resulted, which was set by pressing

additional CO_2 or discharging excess gas to exactly 5 bar total pressure at given temperature.

The duration of the corrosion experiment was four days. To complete the experiment, the heat transfer medium was drained and the autoclave was quickly opened after an approximately 10 minute cooling phase and relaxation to ambient pressure. The mild steel ring was then disassembled and rinsed with methanol, dried with air and then weighed out. This was considered as the mass of the sample after the test and before treatment (m_2). A solution sample was taken from the experiment solution for measuring the pH value and the Fe^{2+} content.

Determination of the pH value of the tested solution

After each experiment, the pH of the solution was measured at normal pressure and ambient temperature using pH meter. The content of dissolved CO_2 was largely reduced to the equilibrium.

Evaluation of mass removal rate (Corrosion rate)

To quantify the results of the experiments, the removal rate of the sample was determined. According to DIN (50900), the corrosion rate is defined as the mass removed within one year [8].

Corrosion rate (Removal rate) in (mm/year) =
$$\frac{\Delta m}{(A \times d \times \sigma)} \times 10 \times 365$$

Where:
A = Surface area of the sample in cm^2
d = Test duration in days
σ = Density of the sample in g/cm^3
Δm = the mass loss due to corrosion=m_3-m_1
m_1 = the mass of the test metal ring before the experiment

The **surface layer mass** was determined from the difference between the mass after and before the test of the surface treatment of the tested metal ring (m_3-m_2).

Determination of Fe^{2+} content

The iron content of the test medium was determined photometrical. The Extinction was measured using a DR Lange Photometer LP3W at the wavelength 510 nm. Fe^{2+} ions form a red complex with 1,10-Phenanthroline chloride monohydrate solution at pH values of 3 - 3.5, which can absorb light in the visible region. The pH of the solution to be measured was adjusted by the addition of sodium acetate solution [9,10].

Accordingly, the sample was first mixed with 37% hydrochloric acid, namely 25 ml of sample with 25 ml of HCl. The resulting solution was stirred for 10 min. in the ultrasonic bath in order to dissolve possibly formed iron oxide Fe_2O_3. A part of this solution was then pipetted off and diluted appropriately with distilled water, mixed with the test reagents and measured photometrical. The reagents were:

- 20 ml sodium acetate buffer
- 5 ml of 1, 10-phenanthrolium chloride solution
- 5 ml of hydroxyl ammonium chloride solution

The final solution volume was completed with water to 100 ml. The Fe^{2+} contents of the unknown samples have been determined using a suitable calibration curve which was prepared by means of samples of known iron concentrations.

Surface Treatment of the sample after the experiment

The metal ring was washed at room temperature for 5 minutes in 10% Hydrochloric acid, containing 0.1% propargyl alcohol, in ultrasonic bath. If the sample was not yet clean, it was stained again for 5 minutes with the same solution after short brushing with a plastic brush.

The sample was then rinsed with tap water, neutralized with a saturated calcium hydroxide solution, rinsed with distilled water, dried over methanol and weighed. This gave the mass of the sample after the test and after treatment (m_3). The masses m_1, m_2 and m_3 were used for the determination of the top layer mass and the mass loss by corrosion.

Results and Discussion

According to the experimental conditions: salt concentration, temperature, surface layer, and the inhibitor ratio, mass removal, pH of

the experimental solution, corrosion rate, and the Fe^{2+} concentration were evaluated as above described in the experimental section. Table (1) shows obtained results of the seven corrosion experiments (T_0-T_6). Generally, all accomplished experiments showed that the corrosion rates increased with increasing chloride and high temperatures. Experiment 1 Fig.(2) showed that the addition of the Dodiscale V3962 inhibitor, in addition to the Dodigen 481, drastically reduced the rate of corrosion for sample T_1 at the temperature of 130°C. In contrast, the addition of Dodiscale

V3962 deteriorated the corrosion rate by half in experiment 2, when the temperature is reduced from 130°C into 90°C. This behaviour shows that Dodiscale V3962 favourably works at high temperature (130°C) in comparison with 90°C. This behaviour might be due to the formation of solid surface mass layer at 130 °C and it is also reflected when the temperature changed from 90°C to 130°C in experiment 4, while the increment of inhibitor ratio remains constant.

Table (1)
Experimental conditions and results of the corrosion study; light rows indicate the varied conditions; shaded rows indicate the results. time = four days.

Experimental Conditions (T= test)	Sample No.						
	T_0	T_1	T_2	T_3	T_4	T_5	T_6
Total chloride concentration g/L	180	180	180	180	0.6	0.6	0.6
T/°C	130	130	90	90	90	130	130
DO 481	1000	1000	300	1000	300	1000	1000
Dodiscale V3962	0	100	100	0	0	0	100
Mass removal g	2.4	1.0	1.00	0.47	0.13	1.15	0.82
Surface layer g/cm^2	15.5	6.6	7.9	4.7	1.67	0.95	9.42
Corrosion rate mm/a	2.4	0.7	0.70	0.33	0.09	1.16	0.62
pH	3	4.8	4.7	5.0	6.3	6	6.9
Fe^{2+} g/L	1.7	1.0	0.90	0.44	0	0	0
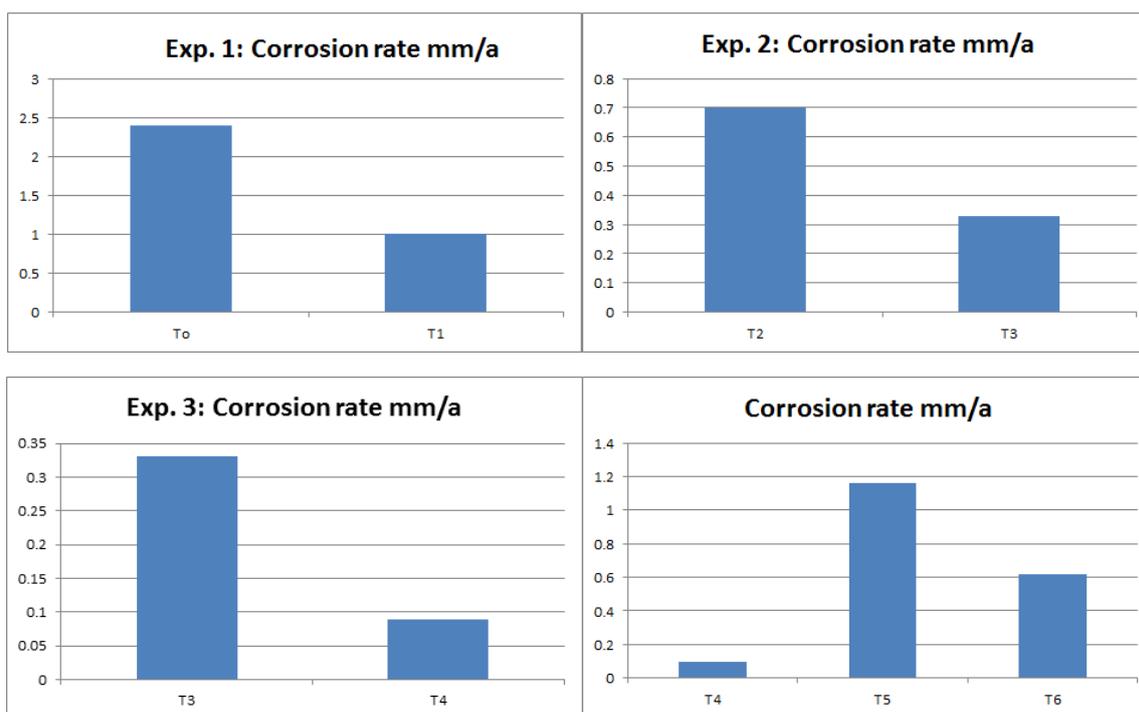
Fig.(2): Calculated corrosion rate found in the corrosion experiments of the studied mild steel rings according to Table (1).

According to the following equation, the electrical conductivity is increased with higher chloride concentration:

Where:

$X = F \times (z_i \times c_i \times u_i)$

F: Farady constant = 96.489 (C / g × eq.)

c_i = concentration of the ionic species i (g × mol / cm^3)

U_i = mobility of the ionic species i (cm^2.v^{-1}.s^{-1})

z_i = ionic charge

eq. = equivalent

Thus, accelerated electrochemical reaction increases the corrosion rate on the metal surface. This effect is ~~refluxed~~ reflected when the chloride ion concentration sank down from 180 to 0.6 g/L in experiment 3.

According to the equation

$$Fe(H_2O)_6^{2+} + H_2O \rightleftharpoons Fe(H_2O)_5OH^+ + H_3O^+$$

As expected pH value of the solution will drop in the solution with higher Fe^{2+} concentration due to the formation of H_3O^+. In all achieved experiments have been observed that acidic pH values were correlated also with high corrosion rates.

For further explanation, Fig.(3) showed all the samples assembled together to obtain another sight of view to analyse the variation of rate of corrosion with respect for experimental conditions. As mentioned above, the increase of chloride ion concentration from 0.6 in the sample T_4 to 180 g/L in T_3 increase the corrosion rate. The corrosion rate remains ascending in T_2 due to contrary acting of Dodiscale V3762 as additional inhibitor at low temperature (90°C). Surprisingly, the same observation is seen by increasing the temperature from 90 °C in sample T_3 to 130°C in T_6 despite the lower chloride concentration (0.6 g/L). The corrosion rates of T_1 and T_2 are the same which means that the temperature change compensates the change in inhibitor ratio at constant chloride concentration. The corrosion rate in the sample T_o increases drastically due to absent of the inhibitor Dodiscale V3762 at high temperature (130°C).
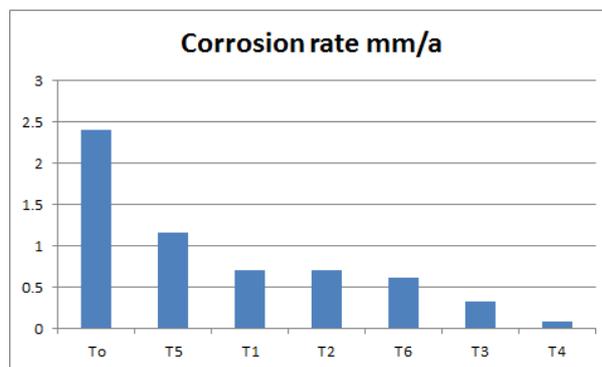
Fig.(3): Arranged experimental corrosion rates of the tested samples after their strength from Table (1).

Optical Evaluation of the surface and cavity corrosion

The corrosion damage of the tested samples is assessed using polarizing microscope at different magnification values as showed in Table (2). The following corrosion strength is also found:

The Strength of corrosion damage in cavities is observed as follows:

$T_3, T_2 > T_5, T_0 > T_1, T_6 > T_4$

The Strength of corrosion damage on metal surface is noticed as follows:

$T_0 > T_5, T_6 > T_1 > T_2, T_3, T_4$

Table (2)
Optical evaluation of the corrosion of tested samples.

T_0		• At cavity considerable erosive removal might be due to high flow vortexes; At the surface Traces of localized corrosion behind the edges
T_1		• At the cavity, slightly damaged especially behind edge; Uniformly mass removal / light hole corrosion, especially behind edge
T_2		• At the cavity, severe erosive damage, especially behind edge; Uniformly mass removal / hole corrosion only on or behind edges
T_3		• At the cavity, significant erosive damage • The corrosion hole behind edges more uniform than it in T_2; At the surface, uniformly mass removal / hole corrosion only around edges
T_4		• At the surface, uniformly hole corrosion short behind edges; Pits uniformly on surface / especially behind edges
T_5		• uniformly erosion, especially behind edge • erosive pits on the entire surface
T_6		• Slightly small pits behind leading edge • Slightly damage / pits behind the leading edge

Conclusion

According to the results of this work it can be concluded that flow induced corrosion is a serious problem. It is demonstrated that high temperatures, high chloride concentrations and high flow rates are the main reasons for the strong flow induced corrosion (test sample T_0). All other test samples showed lower corrosion rates due to addition of Dodiscale V3762 in addition to Dodigen 481 or reduction of chloride ion concentration or temperatures. It is established that Dodiscale V3962 works favourably at high temperatures as in (T_1 and T_6).

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